On transient hot-wire measurement of the thermal conductivity of electrolytic solutions

Baruël, P.

Publication date:
1972

Document Version
Publisher's PDF, also known as Version of record

Risø Report No. 264

Risø Report No. 264

Danish Atomic Energy Commission

Research Establishment Risø

On Transient Hot-Wire Measurement of the Thermal Conductivity of Electrolytic Solutions

by P. Baruël

July 1972

Sales distributors: Jul. Gjellerup, 87, Sølvgade, DK-1307 Copenhagen K, Denmark

Available on exchange from: Library, Danish Atomic Energy Commission, Risø, DK-4000 Roskilde, Denmark

U. D. C.
536.2.08:541.135.2

On Transient Hot-Wire Measurement of the Thermal Conductivity of Electrolytic Solutions

by

P. Baruël

Danish Atomic Energy Commission
Research Establishment Risø
Engineering Department

Abstract

In its "classical" form the transient hot-wire method for measurement of the thermal conductivity of liquids is not suitable for measurements on electrolytic solutions. In this report is described a new modification of the method, permitting measurements on all electrolytic solutions whose decomposition voltage is not quite extremely low (i. e. a few tenths of volts). Till now extension of the method to include measurements on electrolytes has as far as the author knows only been carried through in 2 works, namely by Alas and van der Held et al., the hot wire having been surrounded with an electrically insulating layer. The latter work was later revoked by one of the authors (in co-operation with others). For practical and theoretical reasons Alas uses a thin layer that is dissolved by bases, and that work therefore confines itself to measurements on solutions of salts.

In the present work the electrical insulation round the hot wire is avoided by modification of the measuring cell and the circuit so that the voltage applied to the cell is made to balance with the counter-electromotive force from the electrolytic polarization when a short pulse of current has passed through the liquid. A naked wire can therefore be used in the liquid, which, when balance has been obtained, cannot carry electric current.

A technique has been worked out for "blank experiments" in which the platinum hot wire is replaced by a manganin wire. In such blank experiments electric disturbances at measurement on electrolytic solutions will reveal themselves if they are present.

For experimental verification of the applicability of the method measurements were made on aqueous solutions of KBr, NaCl, NaOH, and H_2SO_4, all in the concentrations 0.5, 1, 1.5, and 2 N. For most of these the thermal conductivity is known from the literature, measured by other methods. The agreement is good. The method can be used on the strongest bases, e.g. about 20 N NaOH, as well as on acids and salt solutions.

The present report builds upon an earlier report by the same author, which contains the necessary circuit analysis and presents the method of calculation. This method differs somewhat from those of earlier authors because the modification necessitated a break with the "classical" principle that the thinnest possible wire (e.g. 20 μm in diameter) should be used. In this work a wire diameter of 500 μm is used. This further resulted in a very robust cell construction.

ISBN 87 550 0156 4

CONTENTS

I. Purpose and Contents of the Investigation

An earlier work [2] reports a number of investigations on the use of the transient hot-wire method for measurement of the thermal conductivity of pure, dielectric liquids. [2] is the basis of the present report.

The mentioned method has in the past decades been used more and more widely for measurement on dielectric liquids, and its principle is broadly outlined in [2], section I. It is as follows. The liquid is filled into a cylindric cell vertically placed in a thermostat. Along the axis of the cell a hot wire is located. When an electric current is fed into a circuit of which the cell is a component, heat will flow from the wire into the liquid. The better the liquid conducts the heat away from the wire, the more slowly the wire temperature increases. In addition to its function as a source of heat, the wire therefore acts, in most designs, as a resistance thermometer, which makes it possible to register its temperature versus time curve by means of a recorder built into the circuit. The wire temperature can also be measured by means of a thermocouple. From the curve registered, and from certain other measurements in the system, the thermal conductivity of the liquid can be deduced according to the theory of the method.

In its original "classical" layout the method is not suitable for measurement on electrolytic solutions. In spite of the fact that certain advantages are often claimed for this method, such as those of being "elegant", fast, and convenient, amazingly few attempts have been made to expand it for measurements on electrolytic solutions since it was introduced in 1931 by Stålhane and Pyk [9] and refined in 1938 by Eucken and Englert [5]. 'Attempts at expansion' are here taken to mean: actually presented works on the theory and practice of such an expansion. A suggestion for the accomplishment of this expansion is often found in the literature, namely: the hot wire should be surrounded with an electrically insulating coating. The only two actually presented works known to the author on the expansion of the transient hot-wire method to comprise also electrolytes, namely one by van der Held and van Drunen [10] from 1949 and one by Alas [1] from 1967, are also built upon this idea. It can presumably be established that in the literature it has till now been taken for granted that use of an electrically insulating layer is the only possibility of expansion*). Thus van

*) The present author knows of no exceptions.

der Held and van Drunen say in their above-mentioned work from 1949 (page 868):

"Not only the chemical activity of some liquids but also phenomena like polarisation and electrophorese made it impossible to use the bare wire in the liquid."

In his 1967-work page 12 Alas says that "die Forderung nach einer Schutzschicht" is "selbstverständlich". In another connection Alas also quotes a work by Bryngdahl in which electrical insulation is stated to be the only possible solution. (Bryngdahl only mentions the possibility of electrolyte measurements by the method but does not perform any work on such measurements.)

As for the two actually presented works [10] and [1] that use an electrically insulating layer, [10] was revoked by van der Held in co-operation with Hardebol and Kalshoven in 1953 [11], and in [1] (1967) Alas found it necessary to use a very thin layer of a material that is dissolved by bases. According to Alas's express statements this means that measurements on bases cannot be made - even though one might imagine that the short duration of the measurements nevertheless made measurements on bases possible when the layer is changed sufficiently often.

The present work mainly reports the experimental part of an investigation begun at the end of 1966 at the Danish Atomic Energy Commission Research Establishment Risø and - after a fairly long interruption - finished in mid-1970 at the same place. In this work it is demonstrated that cell and circuit can be modified so that measurements can be made on a very comprehensive range of bases, salts, and acids without introduction of an electrically insulating layer round the hot wire. The work was prompted by an inquiry from Danish industry to the research establishment. The establishment received samples of liquids, and the inquirer desired their thermal conductivity measured in an apparatus built for hot-wire measurement. These measurements were not possible because the samples proved to be electrolytically conductive, and the apparatus had been built to be used for organic reactor coolants. It was therefore obvious to try to modify apparatus and method so that measurements can be made on electrolytic solutions as well as on dielectric liquids.

The idea of omitting the electrical insulation round the hot wire arose from a feeling that this insulation will give rise to difficulties - which was later confirmed in several ways through Alas's work - and from an intuitive idea that the electrolytical polarization may be considered as a counter-

electromotive force which it must be possible to make balance with the voltage applied to the cell. The electric current will then automatically be barred from passing through the liquid. If this can be obtained sufficiently fast, the cell with the electrolytic solution can be considered as if the liquid were dielectric for a sufficiently long period for measuring without complications.

However, matters are not quite as simple as outlined here. A more detailed analysis is necessary to ascertain that incalculable sources of error do not occur. Along with the experiments the work has therefore to a wide extent been guided by theoretical considerations. For practical reasons it has, however, been necessary to limit the discussion of these matters to a minimum in this report so that only in section II a short, necessary link-up to [2] is made. The author hopes to be able to go more thoroughly into the theoretical aspects in a later report, but seen from a certain angle it is quite reasonable to present the experimental part of the work as a fairly completed work. This is justified because, as will appear from the following, a technique of "blank experiments" was worked out that ensures that disturbing errors of electric origin do not occur in an actual case of measurement on an electrolyte.

The author wishes to stress that with the experiments made it was not the intention to construct an apparatus suitable for the fastest and most accurate routine measurements possible. As for quickness, the author did not have the possibility of using full automation. For treatment of the data a semi-automatic method was therefore used that is based upon manual measuring out of recorded voltage versus time diagrams as described in [2], section VI. As far as accuracy is concerned the main purpose was to establish with sufficient accuracy that the developed modification of the method to comprise electrolytes is just as correct as is the "classical" version of the method for measurement on dielectric liquids. In [2], section VII, are given some examples from the literature of the demands of accuracy of thermal conductivity determinations made for engineering purposes and for basic studies. According to these examples, the accuracy obtained in the present work is more than sufficient for engineering purposes such as those that prompted the work. For basic purposes an attempt should perhaps be made to improve the accuracy (about $\pm$ 1% for a single determination). There are various possibilities of doing this, and the author hopes in a later work to be able to carry through full automation as well as the possibilities of refining the apparatus itself. It must of course also be possible to use the apparatus for measurement on dielectric liquids, and the principle of such measurements has to some extent been described in [2]. In

the present report the apparatus and its use are described in detail, and results are given of measurements on aqueous solutions of KBr, NaCl, $CuSO_4$, NaOH, and H_2SO_4, each in the concentrations 0.5, 1, 1.5, and 2N.

In the above-mentioned section VII of [2] there are a few short remarks on mutual evaluations of various methods for measurement of thermal conductivity. In agreement with these remarks it is not the intention to claim that the present method is "better" than that of Alas [1] or others that might be presented with layers of electrical insulation round the hot wire. It may, on the other hand, supplement such as its field of application may be different,so that what is covered by this method may not be covered by the "insulation method" and vice versa. Where the fields of application overlap, the two methods may be used for mutual control, which is an essential side of scientific method.

From a practical point o. view the modification, as it has been developed at the present stage, may have some advantages over the "classical" version modified with insulation coatings. With its "thick" wire (cf. [2] page 9) the cell is more sturdy and simple than is e. g. Alas's. Moreover, the coating must not be repeatedly checked for leakages. If an extremely thin coat is used - e. g. a monomolecular layer - the slightest solubility in the electrolyte will probably be fatal. If a thicker coat is used, the theory that connects the quantities measured with the thermal conductivity sought will become more complicated as will be outlined in section IV of this report.

II. Theoretical Problems at Measurement of the Thermal Conductivity of Electrolytic Solutions

2). General Remarks

In [2], section II, the general, theoretical foundation of heat conduction in pure, dielectric liquids was discussed. For such liquids it is quite generally found that

$$\lambda \nabla^2 T - \rho c_p \frac{\partial T}{\partial t} = \rho c_p \vec{v} \cdot \operatorname{grad} T - \operatorname{grad} T \cdot \operatorname{grad} \lambda - \alpha T \frac{dp}{dt} - \Phi, \quad (1)$$

where

λ = thermal conductivity

ρ = density

T = temperature

c_p = specific heat at constant pressure

t = time

∇^2 refers to space coordinates

$\vec{v}$ = velocity of the liquid

'ϕ' = abbreviation introduced for term owing to internal friction.

This equation is eq. (10) in [2], and it builds upon well-known presumptions, e. g. on the energy equation and Fourier's law

$$\vec{j}_u = -\lambda \, \mathrm{grad} T \, , \tag{2}$$

where $\vec{j}_u$ is the diffusion flow density for non-mechanical energy. (2) may be considered as the definition of λ for pure (dielectric) substances.

As the starting point for investigations on transient λ-measurement for pure, fluid substances the "heat flow equation"

$$\lambda \nabla^2 T - \rho c_p \frac{\partial T}{\partial t} = 0 \tag{1a}$$

is always used in the literature on this subject. This equation is obtained from (1) by neglecting the right-hand side. In [2], section II, it was shown that this approximation is applicable for transient hot-wire measurement with a vertical hot wire.

In the literature on λ-measurement it is further usual to accept the presumptions of (1a) - among these (2) - when proceeding to measurement on mixtures. λ is thus still considered as being well defined through (2), although the theory is complicated by the fact that (in principle) thermal diffusion may occur in mixtures. If the mixtures are electrolytically conductive, it is assumed that the essential point is simply to avoid electrolysis during the measurements, which may then be performed as on pure liquids. Electrolysis is avoided by using electrically insulated heat sources in the types of apparatus where the temperature differences are established electrically. It is self-evident that electrolysis must not occur, among other things because it would disturb the electrical recordings, and because it will often result in production of gaseous substances. The heat flow must of course not encounter bubbles on its passage through the liquid.

As mentioned on page 7 we shall to a wide extent ignore the theoretical complications when proceeding to electrolytic solutions. We shall, for

instance, present the experimental part of the present work on the assumption that (like most dielectric liquid mixtures) electrolytic solutions may in practice be given a well-defined λ thorugh (2). By so doing, we are in agreement with all literature on the measurement of λ known to the author. Moreover, theoretical considerations also show that generally the complications are without importance.

b). Problems Concerning Transient Hot-Wire Measurement on Electrolytic Solutions Without Electrical Insulation Round the Hot Wire

As mentioned in section I, the aim of this work is to make it possible to measure on electrolytic solutions by the transient hot-wire method without electrical insulation of the hot wire.

We shall first imagine the hot wire removed and the cell filled with an electrolytic solution. The cell then makes up an electrolysis system with the wire retainers as electrodes. If a potential difference, $\Delta\varphi$, is applied to them, an electric field, $\vec{E}$, is established in the liquid. From physical chemistry it is known that if $\Delta\varphi$ \ the decomposition voltage δ of the electrolyte, we shall have a continuous electrolysis concurrently with chemical processes in the interfacial layers between the retainers and the electrolyte. If $\Delta\varphi < \delta$, the electrolyte, however, does not remain free of current after application of $\Delta\varphi$. This can be seen from modern non-equilibrium thermodynamics, which give a general expression for the electric current density in electrically conducting phases. As we do not treat thermal diffusion and at the present not convection either, we assume that temperature gradients and mechanical motion in the electrolytic solution may be ignored during the time of consideration.

For the electric current density in the solution the above-mentioned theory then gives an expression of the form

$$\vec{i} = \sigma \vec{E} + \Sigma \Lambda \operatorname{grad} \mu \,, \qquad (3)$$

where

$\vec{i}$ = electric current density

μ = the chemical potentials of the components

'Σ' refers to summation over chemical components

σ and Λ's are coefficients determined by the intensive properties of the system such as temperature and composition.

Immediately after $\Delta\varphi$ has been applied we have, however, all $\operatorname{grad}\mu = \vec{0}$

because the liquid is homogeneous and we presupposed grad T $\simeq \vec{0}$ and mechanical equilibrium. The last-mentioned condition corresponds to *) grad p = $\vec{0}$, where p = pressure.

Eq. (3), which does not presuppose anything about the value of the applied voltage $\Delta\varphi$ over the cell, thus shows that although we do not have continuous electrolysis, we must have

$$\vec{i} \neq \vec{0} \text{ in the electrolyte}$$

because $\vec{E} \neq \vec{0}$ in the electrolyte.

This means that ions flow to the electrodes where they make up part of the interfacial layers between them and the electrolyte. As, however, continuous chemical reactions do not occur below the decomposition voltage, $\vec{i}$ must again become $\vec{0}$ after a certain time as only limited amounts of substances can be transported to and from the interfacial layers without chemical processes in or passage through these layers. We thus have a pulse of current through the liquid that fades out, and end up with balance between the applied voltage and the potential differences that occur in the interfacial layers on account of the ion transports to and from them.

We now imagine the wire inserted in the retainers, i.e. the electrodes connected with a metallic, conductive wire. The cell is then filled with an electrolytic solution, and a voltage $<$ the decomposition voltage is applied to it. The fact that the current in the liquid must also in this case die out seems now to lead to a paradox. One might namely be inclined to reason as follows: In the wire there is constantly an electric current in the axial direction at the wire surface. As the wire is chemically homogeneous and has no axial temperature differences, μ for the electrons is constant in axial direction, z (i.e. $\frac{\partial \mu}{\partial z} = 0$). (3), which applies to arbitrary electrically conductive phases, therefore shows that there is an electric field for which $E_z = \frac{i_z}{\sigma} \neq 0$ in the wire at the surface, subscript 'z' indicating components in the z-direction. As a well-known jump condition to the Maxwellian equations says that the component of $\vec{E}$ tangential to an interface is continuous, i.e. it is the same on both sides of the interface, we constantly have $E_z \neq 0$ in the electrolyte. As the electrolyte does not show z-components for the grad μ's either during the experiment this

*) On account of the electroneutrality condition $\vec{E}$ does not contribute to the force density.

means that in the electrolyte we have $i_z = \sigma E_z \neq 0$. So it seems as if the electrolyte must continue to carry current. However, this reasoning is not correct. The proof generally given for the tangential component of $\vec{E}$ being continuous when passing an interface, presupposes that the interface is homogeneous perpendicularly to its normal direction. Therefore there is nothing to prevent a situation beginning as outlined in fig. 1, but ending with $\vec{i} = \vec{0}$ in the liquid:

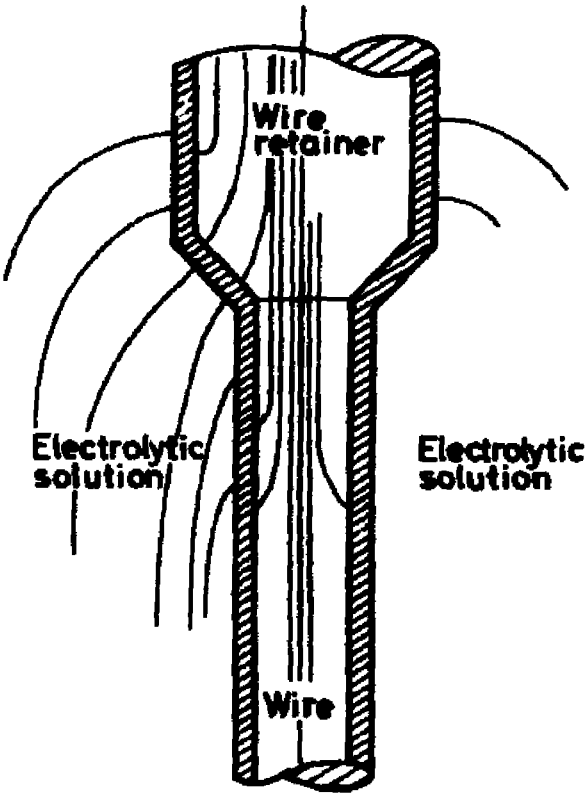


Fig. 1

Fig. 1 shows the instantaneous electrical lines of flow immediately after the current has been switched on. The interfacial phases are indicated by hatching and by a certain thickness that naturally has not been drawn to a reasonable scale. The lines of flow should continue into the interfacial layers and end there if chemical processes do not occur, but for the sake of clarity they have been interrupted at the boundaries. In the wire the current is due to electron transport. In the electrolyte the instantaneous electrical lines of flow "result" from flows of anions and of cations transported in opposite directions. The interfaces between wire (or retainers) and electrolyte therefore become inhomogeneous in the z-direction, while the current passes through the electrolyte, and a jump is built up in E_z from wire (retainers) to liquid. As the experiment is carried out below the decomposition voltage, δ, this must - as before when the wire was removed - result in balance in the liquid.

c). Investigation of the Disturbing Effect of the Pulses of Current on the Recordings

We shall now investigate the importance for the recordings of such a pulse of current in the liquid if measurements on an electrolyte are attempted below b with an electrically uninsulated wire and in accordance with the simple theory for dielectrics in [2], sections V and VI. Incidentally, we may note that the addition 'with electrically uninsulated wire' is in principle unnecessary as even if the wire was electrically insulated, there would, nevertheless, occur a pulse of current in the liquid. If it is insulated with e. g. a monomolecular layer, a single layer of dipoles has simply been inserted in the interfacial layer, and these dipoles orient themselves during the pulse of current. If, therefore, disturbances can be demonstrated in the recordings from the pulse of current with electrically uninsulated wire, such disturbances will in principle also occur if electric insulation is used. (The pulse of current is, however, not mentioned by any author who recommends or uses the last-mentioned possibility of modification of the method for measurement on electrolytes).

We shall now carry through the desired investigation concerning the registrations under the following assumptions:

1) The pulse of current in the liquid and the radial pulse of current in the wire fade out within such a short time that convective phenomena may be ignored during the passing off of the pulse. It may e. g. be a question of 1 or 2 seconds (cf. the experiments with earthmoss-seeds in [2], page 16).

2) Within the time considered, concentration gradients and temperature gradients do not prevent the use of (3) on the form

$$\vec{i} = \sigma \vec{E}$$

in the metal as well as in the electrolyte. The term $\Lambda \operatorname{grad} \mu$ in (3) is thus negligible.

We shall now use a well-known jump condition to the Maxwellian equation, namely

$$\left[\vec{i} + \frac{\partial \vec{D}}{\partial t} \right]_n = 0 ,$$

where '$[\ \ ]_n$' means jump of a vector component perpendicular to an inter-

face, $\vec{D}$ is the dielectric induction, and $\vec{i}$ as usual the electric current density. We may, for instance, consider one half of the cell resulting from a cross section laid through the middle. By integration of the mentioned jump condition over the surfaces of a retainer and a wire half with the area element do we find

$$I^* + \int \frac{\partial D_n^*}{\partial t}\, do = I_L + \int \frac{\partial D_n}{\partial t}\, do, \tag{4}$$

where

I^* = strength of the radial pulse in the wire

I_L = current in the liquid

Subscript 'n' indicates component normal to the wire surface

D_n^* = the n-component of $\vec{D}$ on the metal side of the wire surface.

With '*' always referring to the metal side we have

$$\left.\begin{aligned} \vec{D} &= \varepsilon \vec{E} \text{ in the liquid} \\ \vec{D}^* &= \varepsilon^* \vec{E}^* \text{ in the metal} \end{aligned}\right\} \tag{5}$$

and according to our assumptions

$$\left.\begin{aligned} \vec{i} &= \sigma \vec{E} \text{ in the liquid} \\ \vec{i}^* &= \sigma^* \vec{E}^* \text{ in the metal.} \end{aligned}\right\} \tag{6}$$

In (5) and (6) ε, ε^*, σ, and σ^* are functions of pressure, temperature, and composition, and they are constants in the bulk phases.

If (5) and (6) are substituted into (4), we get

$$I^* + \frac{\varepsilon^*}{\sigma^*} \frac{dI^*}{dt} = I_L + \frac{\varepsilon}{\sigma} \frac{dI_L}{dt} \,. \tag{7}$$

In the Appendix examples are given of the order of magnitude of $\frac{\varepsilon^*}{\sigma^*}$ and $\frac{\varepsilon}{\sigma}$. Generally they are extremely small. When $\left|\frac{dI^*}{dt}\right|$ and $\left|\frac{dI}{dt}\right|$ are not quite extremely high circumstances are consequently as if the current passes through the interfacial layers:

$$I^* \simeq I_L \,. \tag{8}$$

It is then evident that the cell may be illustrated by a diagram as in fig. 2 - where the interfaces appear as electromotive forces - and the following expression for the cell voltage may then be written down

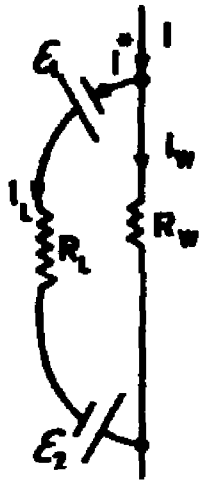


Fig.2

$$\left.\begin{aligned} \Delta\varphi_c &= R_L I_L + \mathcal{E} \\ \Delta\varphi_c &= R_W I_W , \end{aligned}\right\} \qquad (9)$$

where I_W, as will be seen, is the current through the wire, I_L is the current through the liquid, R_W and R_L are the resistance of the wire and of the liquid column respectively, and $\mathcal{E} = \mathcal{E}_1 + \mathcal{E}_2$ = the total counter-electromotive force in the interfacial layers.

In fig. 2 the interfacial layers are represented by electromotive forces. Another view, found in the literature, is that when $\Delta\varphi < \delta$, they should be represented by condensers. This would also explain potential differences over the interfacial layers. It is very difficult and space-consuming to give an account of how these layers can be visualized if kinetic phenomena (e.g. how the current pulses pass off) are to be calculated under acceptable, non-idealized conditions, for instance also with regard to induction phenomena. The author hopes, as mentioned earlier, to get an opportunity to write a report treating the theoretical aspects of the present work in more detail. In such a report it would, among other things, be possible to treat more explicitly the permissibility of using fig. 2 as a "model" of the system. Here we shall simply lay down that (9) - that does not explicitly concern kinetic aspects - is valid irrespective of whether the interfacial layers are considered as electromotive forces (without an inner ohmic resistance) or as condensers (or as both in series), and we shall accept (9) under assumptions 1) and 2).

From fig. 2 it is seen that when I is the current fed to the cell, we have

$$I = I^* + I_W ,$$

and (8) and (9) give

$$I = I_W + I_L = \frac{\Delta\varphi_c - \mathcal{E}}{R_L} + \frac{\Delta\varphi_c}{R_W} = \frac{\Delta\varphi_c}{R_C} ,$$

where R_C = the total cell resistance.

Thus we finally find

$$R_C = \frac{R_W R_L}{R_L + R_W \left(1 - \frac{\mathcal{E}}{\Delta\varphi_c}\right)} .$$

This expression becomes a little simpler if we introduce

$$\left.\begin{aligned} f &= \frac{R_W}{R_L} \\ p &= 1 - \frac{\mathcal{E}}{\Delta\varphi_c} . \end{aligned}\right\} \qquad (10)$$

It then reads

$$R_C = \frac{R_W}{1+fp} .$$

It is seen that not until $\mathcal{E}$ and $\Delta\varphi_{\mathcal{E}}$ balance, i.e. not until the pulses of current have passed (i.e. when $I_L = I^{\mathcal{E}} = 0$), do we have $p = 0$ and $R_C = R_W$ as is presupposed in the elementary circuit analysis in [2], section V.

Thus, if this analysis is used, correct results are only obtained if the liquid on which measurements are made is dielectric, unless the pulses of current have passed before the recordings are used. What is registered on the recorder is changes of R_C, but changes of R_W is what is actually required. (10) therefore shows that as p varies during the pulses of current, these cause errors in the recorder registrations, and the essential thing is to make these errors as small as possible and to make them disappear as fast as possible.

As will be seen from what has been said immediately above, a certain period of waiting must be expected before the recordings can be used, which is not possible until the pulses of current have died out. Among others, the question is now: Will there be time enough for the measurement before the convection disturbs the heat transport from the wire appreciably? In [2], page 15, it was shown for a pure liquid that it is not possible to have heat flow radially out from the wire together with mechanical equilibrium, i.e. together with freedom of convection. For that demonstration we used the mechanical equilibrium condition together with the fact that the liquid has an equation of state $T = T(\rho, p)$ where T = temperature, ρ = density, and p = pressure. For an electrolytic solution the equilibrium condition will,

in agreement with a footnote on page 11, be the same as for a pure liquid. But the equation of state for the electrolyte has the form $T = T(\rho, p, x_1, x_2 \ldots\ldots)$ where x_1, x_2 ..... are mole fractions of components.

The mole fractions can, however, only be changed by diffusion or chemical processes. Chemical processes are disregarded in these considerations that only concern non-reacting solutions, and the x's will therefore not be changed until after a period of thermal diffusion (and current passage). During the measurement period changes that matter hardly occur. In other words, the x's may be considered constant - at any rate during the time immediately after the current to the cell has been switched on - and we have as for pure liquids: the convection must occur immediately. The result of the detailed investigations on the convection in pure liquids by hot-wire measurement in [2], section III, may now be applied directly to electrolytic solutions: also for electrolytic solutions we have equations of motion of the Navier - Stokes type which were a presumption for the treatment of convection in [2] and on account of the electroneutrality condition there is no electro-magnetic contribution to the force density. (It must be permissible to ignore magneto-hydrodynamic complications.)

Moreover - for the express purpose of the present investigations - experiments were also made with earthmoss-seeds in electrolytic solutions, although these are not pure liquids, when [2], section III, was worked out.

The result of this section of [2] was that just in hot-wire cells with vertical wire the convection does not disturb measurement of λ as long as it is laminar. This is due to certain geometrical aspects concerning the velocity field and the grad T field in such cells. For "ordinary" liquids laminar flow may during measuring be taken to last about 8-10 seconds, and even when the recordings made during the first few seconds are disregarded, there is more than ample material for the calculation of λ.

If, therefore, arrangements can be made so that the pulse of current in the electrolyte - which as shown disturbs the recordings - has died out after a few seconds or less, disturbances from convection can be disregarded, and in that case the desired modification of the method seems possible.

Consequently it would be extremely interesting to be able to calculate the passing off of the current pulses. To do this without very idealized presumptions is, however, difficult. It will therefore be necessary to resort to experimental investigations. How this can be done is described in the following section.

III. Experimental Investigation of the Pulses of Current by Means of "Blank Experiments". Demonstration of Feasibility of the Modification

During the current pulses electrons flow to and away from the metal side of the interfacial layers between wire (or retainers) and solution. Ions flow to and away from the liquid side of the layers. Speaking of fig. 1, we assumed that chemical processes did not occur in the interfacial layers. But even if one operates below the decomposition voltage, δ, it is not certain that polarization takes such an "ideal" course through "non-faradayan pulses" entirely without the participation of chemical processes. It is conceivable that such processes occur to a small extent without the saturation concentrations of the products being exceeded, i. e. without formation of new phases. If chemical processes occur they will cease after some time as otherwise the voltage applied should be higher than δ. But the processes may delay the fading out of the pulses which are initiated in a "non-faradayan" way. If chemical processes participate, the equilibrium, finally achieved when operating below δ, will not be thermodynamically stable, but only partial and approximate because the products will diffuse away from the boundary layers in which they are produced, but these diffusion processes can probably be neglected during the measurement period. Whether "ideal polarization" is established or chemical processes participate, the formulae (10) is arrived at. In the latter case, the flow lines in fig. 1 can be imagined drawn through the boundary layers. In the formulae (10), the variable p appears when the cell is filled up with an electrolytic solution, and in the previous section it was shown that the variation of p leads to registration errors. In addition to this source of error comes a revision of the result of the circuit analysis (51), in [2], section V, which is valid for $p = 0$, i. e. for dielectric liquids. The result of the analysis in [2] builds upon the condition $\Delta R_C \ll \Sigma$, where ΔR_C is the resistance variation of the cell during the measurement, and Σ = the sum of the resistances in the bridge. When $p = 0$, ΔR_C is entirely due to the increase in the wire temperature, and ΔR_C could easily be estimated in [2] with the result that the said condition was fulfilled. As ΔR_C is now due to variations in temperature as well as in p, a fresh investigation is apparently needed.

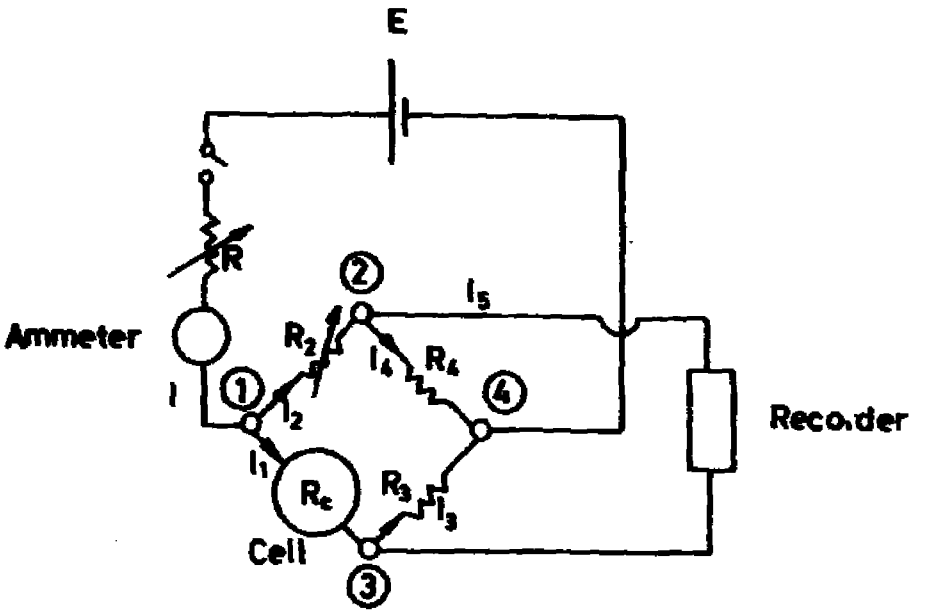

E
R
Ammeter
I
①
②
③
④
R_2
I_2
I_5
I_4
R_4
I_1
R_c
R_3
I_3
Cell
Recorder

Fig.3

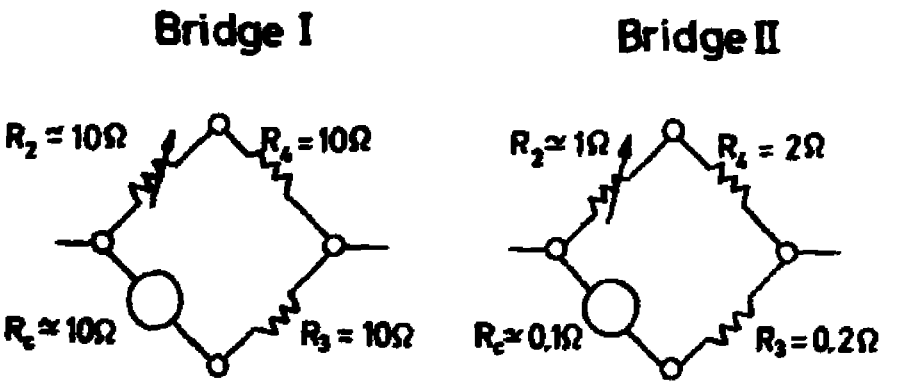

Bridge I
$R_2 \simeq 10\Omega$
$R_4 = 10\Omega$
$R_c \simeq 10\Omega$
$R_3 = 10\Omega$
Bridge II
$R_2 \simeq 1\Omega$
$R_4 = 2\Omega$
$R_c \simeq 0.1\Omega$
$R_3 = 0.2\Omega$

Fig.4

Let us now first imagine that p, which is, according to its definition, lying in the interval $0 \leq p \leq 1$, varies through just this interval during the measurement period. In this case it can be seen that neither of the bridge set-ups I and II previously described in [2], page 39, can be used. This will be demonstrated now. Fig. 3 is a reproduction of fig. 7 in [2] and fig. 4 a reproduction of fig. 8 in [2]. Fig. 3 and fig. 4 show the circuit used and the 2 bridges, respectively, of which No. I was previously used to measure on dielectric liquids in a "classical", i.e. in an unmodified, set-up.

For the sake of convenience, the quantity

$$\xi = fp \tag{11}$$

is introduced into the following, and (10) then gives

$$R_C = \frac{R_W}{1+\xi} \,. \tag{12}$$

On "difference form", (12) can be written

$$\Delta R_C = R_W^o \left(\frac{1}{1+\xi} - \frac{1}{1+\xi_o} \right) + \frac{1}{1+\xi} \Delta R_W \,, \tag{12a}$$

where ΔR_C = the difference between the value corresponding to $\xi = fp$ and the initial value corresponding to $\xi = \xi_o$, i.e. $\Delta R_C = R_C - R_C^o$, the initial value being marked by the index 'o'. 'ΔR_W^o has an analogous meaning.

Thus

$$\Delta R_C = \frac{\xi_o - \xi}{(1+\xi)(1+\xi_o)} R_W^o + \frac{1}{1+\xi} \Delta R_W \tag{13}$$

As said, we now imagine that p runs slowly through the interval $0 \leq p \leq 1$ during the measurement period in such a way that $p = 0$ - i.e. $\xi = 0$ - around its expiry. When a tilde indicates values at the end of the experiment, (13) gives

$$\tilde{\Delta R}_C = R_W^o \frac{f_o}{1+f_o} + \tilde{\Delta R}_W \tag{14}$$

because for $t = 0$, $\xi = \xi_o = f_o p_o = f_o \cdot 1 = f_o$.

Since the liquid column and the wire are equally long, we have

$$f = \frac{R_W}{R_L} = \frac{\sigma_L}{\sigma_W}\,\frac{A_L}{A_W} = \frac{\sigma_L}{\sigma_W}\left(\frac{r_L}{r_W}\right)^2 ,$$

where σ = specific conductivity, A = cross sectional area and r = cross sectional radius. Subscript 'L' refers to the liquid.

In set-up I, one may e. g. have $r_W = 1.5 \cdot 10^{-3}$ cm ("thin wire"), and in II, $r_W = 0.25 \cdot 10^{-1}$ cm ("thick wire").

In both set-ups, a cell cross section with $r_L = 3$ cm is used.

If we e. g. consider a 1N KCl solution, we have $\sigma_L \simeq 10\ \Omega^{-1}m^{-1}$. σ_W is equal to σ for platinum $\simeq 10^7\ \Omega^{-1}m^{-1}$, and one finds - the values applying at about 25°C -

Set-up I: $f_o = 4$

Set-up II: $f_o = 1.4 \cdot 10^{-2}$.

Since R_W^o in I was *) about 16 Ω, this gives according to (14)

$$\begin{aligned} &\text{Set-up I:} \quad \tilde{\Delta R}_C = 13\Omega + \tilde{\Delta R}_W \\ &\text{Set-up II:} \quad \tilde{\Delta R}_C = 1.4 \cdot 10^{-3}\,\Omega + \tilde{\Delta R}_W \end{aligned} \qquad (15)$$

For $\tilde{\Delta R}_W$ it will be reasonable to aim at values as in experiments with pure water, as it is known that these values do not give rise to disturbances from turbulence during the measurement period. According to page 43 in [2], one will thus attempt to obtain

Set-up I: $\tilde{\Delta R}_W \simeq 7.4 \cdot 10^{-2}\ \Omega$

Set-up II: $\tilde{\Delta R}_W \simeq 1.2 \cdot 10^{-3}\ \Omega$.

However, it is ΔR_W that is required; but it is ΔR_C that is recorded. In set-up I $\tilde{\Delta R}_W$ is entirely negligible compared to the contribution of 13 Ω to $\tilde{\Delta R}_C$ from the p variation, and the sensitivity of the recorder must be re-

---

*) Cf. footnote page 43 in [2] where this discrepancy with fig. 8 in [2] is explained. The resistance values in the figure are heavily rounded values, having been used for estimation purposes.

duced considerably to keep the curve on the paper. In set-up II, conditions have apparently improved somewhat; but it cannot be used since no method exists to separate $\tilde{\Delta R}_C$ exactly in the contribution from the p variation (about $1.4 \cdot 10^{-3}$ Ω) and $\tilde{\Delta R}_W$. (Even if one would measure σ_L for each electrolyte, the contribution from the p variation could not be found exactly; because it is only a presupposition serving as an illustration that p varies through the whole interval $0 \leq p \leq 1$ during the measurement). It is therefore of the greatest importance for the carrying out of the modification that it is possible to demonstrate that p varies in a smaller interval.

It appears that this fact involves that the modified set-up II can be used for electrolytic measurements and that set-up I is useless for such purposes. In order to demonstrate this it must be shown how p variations or, more conveniently, ξ variations in the set-ups can be studied experimentally.

If, instead of the platinum wire, a manganin wire with the same resistance is inserted, the change of the wire resistance during the heating will be so small in a period equal to the usual measurement period of λ determinations that it cannot be registered on account of the very weak temperature dependence of the manganin resistance. During such an experiment, which in the following will be termed 'a blank experiment', we therefore have

$$R_W = \text{const.} = R_W^o$$

and according to (12)

$$R_C = \frac{R_W^o}{1+\xi} \qquad \text{for blank experiments.} \tag{16}$$

When ξ (i.e. p) in a blank experiment has reached the value 0, we therefore have

$$R_C = \text{const.},$$

and from this moment the recorder diagram becomes a straight line parallel with the time axis. In a set-up where the formula (42a) of the circuit analysis in [2] is valid, the whole course of ξ during a blank experiment can be inferred from the diagram and from (16). The said formula of [2] rea
when φ is the diagonal voltage in the bridge and the bridge is in balance at

the beginning of the experiment,

$$\varphi = I_o \frac{R_4 \Delta R_C}{\Sigma} \quad ,$$

where I_o is the current read on the ammeter fig. 3.

Let us now tentatively assume that this formula is valid. The question is then whether it is possible from the course of ξ during a blank experiment to infer the course of ξ in an experiment for the determination of λ. The latter experiment will for short be named 'the main experiment'.

For the mentioned inference to be possible it is a condition that the manganin wire does not catalyze the electrode processes positively or negatively compared to the platinum wire. Such a catalysis from the manganin might very well occur. The manganin contains e. g. Cu, and, as is well known, Cu^{++} catalyzes many processes. This possibility may easily be precluded, however: the manganin wire is placed outside the cell between two thick copper blocks without appreciable resistances, as sketched in fig. 5. In the cell the electric current flows through the liquid between the retainers until it fades out. If the retainers are not of platinum, but e. g. of stainless steel as in the apparatuses used, small bits of platinum wire may be inserted in the retainers during the blank experiments so that any catalytic effect from Pt in the main experiments also occur in the blank experiments.

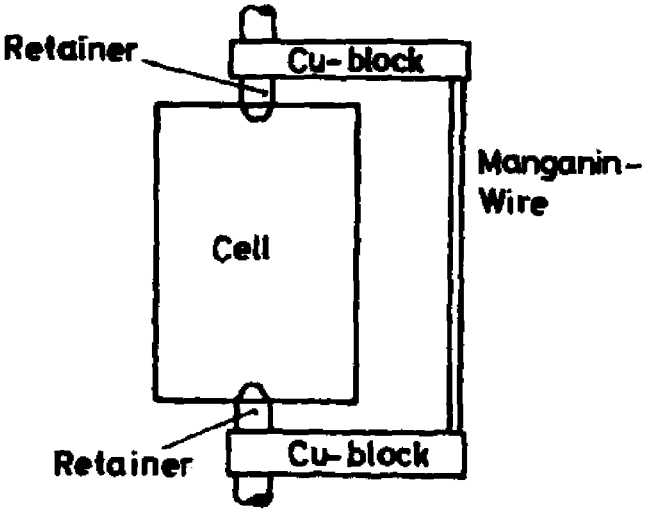


Fig. 5

The whole apparatus fig. 5 must, as in the main experiment with a Pt wire, stand in a water thermostat*) with redistilled water ($\sigma \simeq 0$) for cooling of the manganin wire, which after all does have a very small resistance temperature coefficient.

*) Or an oil thermostat.

That the current in the blank experiments flows between the retainers only and not also from half of a wire to another half of a wire through the liquid as in the main experiments does not mean anything as far as the inferences from blank to main experiments are concerned. This has been shown in a series of experiments where the platinum wire bits mentioned were extended to almost wire halves, which only did not touch each other. The blank curves on the recorder did not change in the least thereby. The course of ξ in its entire extension can hardly be transferred exactly from blank to main experiments, i. a. because the wire in the latter experiments becomes hotter*), which affects the reaction rate. The initial value, ξ_0, or, at least, its order of magnitude can, however, be transferred unchanged, and that is all that is needed.

As far as the forms of the blank curves are concerned, they can - as described in connection with fig. 12 in [2] for experiments for determination of λ for non-electrolytes - lie differently displaced on the recorder paper dependent upon the adjustment of the apparatus at the moment the current is switched on at $t = 0$. With two different adjustments for the same electrolyte the two curves are congruent.

A survey of the forms of the blank curves and their significance is perhaps most easily obtained by imagining that p varies through the interval $0 \leq p \leq 1$ and that the recorder is absolutely perfect, i. e. instantaneously without delay. Figs. 6a and b indicate the forms of two blank curves corresponding to this. t is the time and φ is the registration of the recorder measured in units of voltage. In fig. 6a the bridge is thought adjusted in such a way that $\varphi = 0$ when $p = 0$, i. e. the recorder pen does not deflect when the bridge is balanced, and the liquid column is barred from current passage. $\varphi = 0$ is thus tantamount to the other bridge resistances balancing with the wire alone. When the current to the cell with freshly filled electrolyte is now switched on at $t = 0$ in a blank experiment, the liquid column and wire are suddenly inserted in parallel, and hence an unbalance instantaneously develops and the recorder moves as shown by the "vertical" arrow to a point where $p = 1$. Then p and φ decrease to zero during the registration of the curved line, the liquid column being gradually barred to current by the increasing counter-electromotive force. In fig. 6b the ad-

---

*) In the blank experiments the wire is, as mentioned, placed in a thermostat with circulation.

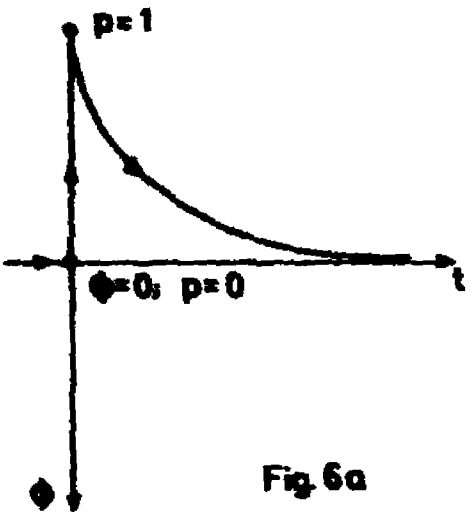


Fig. 6a

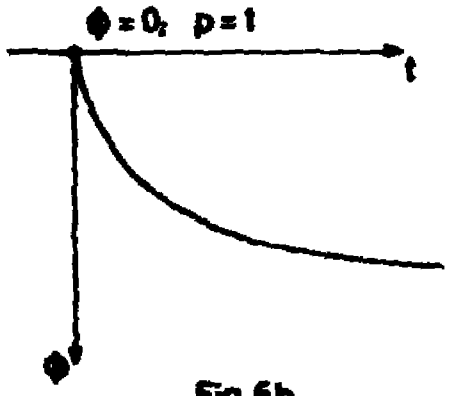


Fig. 6b

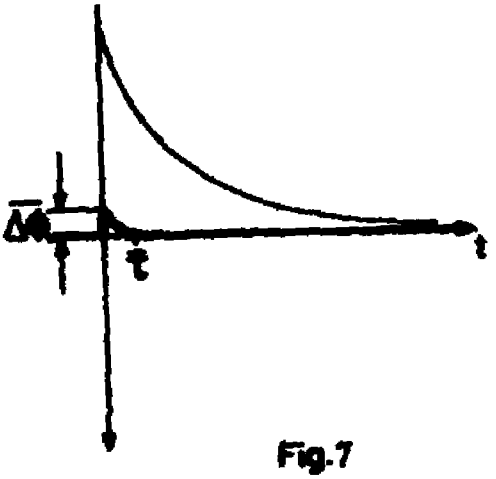


Fig. 7

justment is thought to be such that $\varphi = 0$ at balance of the bridge with wire and liquid column inserted in parallel. At other adjustments it may happen both that the curve comes to lie "higher" than *in* fig. 6a, between the two positions in the figures, as well as "below" the position in fig. 6b.

If p does not vary through the whole of the interval from 0 to 1 during the measurement period but only through a small part of it, the form of the blank curves becomes as indicated in fig. 7 provided the adjustment is as stated in connection with fig. 6a. The curve *from* fig. 6a *is* sketched on fig. 7 in a thin line and the blank curve is fully drawn.

With the *modified* set-up *II*, curves were obtained that correspond to the fully drawn line in fig. 7; however, these curves *might* have an arbitrary, parallel-displaced position in the direction of the φ-axis according to the adjustment, as indicated *in* fig. 8.

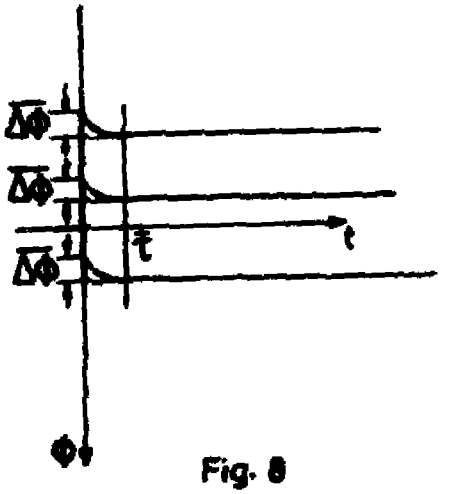


Fig. 8

In the case of set-up I, such experiments in accordance with the above (page 21) could be performed only after an appreciable reduction of the sensitivity of the recorder. Even after this, the curved parts of the diagrams stretch over the whole of the measurement period. For set-up II the initial value of ξ can now be found - in any case as far as the order of magnitude is concerned. For all solutions and currents (which were varied in the interval permitted by the apparatus)

$$\bar{\tau} \; < \; \frac{1}{2} \text{ second}$$

$$\overline{\Delta\varphi} \; < \; 5 \cdot 10^{-5} \text{ volt}$$

were found from the diagrams. The meaning of the symbols provided with bars appears from figs. 7 and 8. The values given are very ample.

In many cases $\bar{\tau}$ was rather about 1/4 s and $\overline{\Delta\varphi}$ about 10 times smaller. Generally, the "jump" corresponding to $\overline{\Delta\varphi}$ in the figures was registered practically "vertical" in the recorder diagrams, i.e. in the direction of the φ-axis, the jump being, with suitable adjustment, extremely short. According to the investigations in [2], section VI, on the inertia of the recorder, the order of magnitude of $\overline{\Delta\varphi}$ can therefore be determined reliably. Let now $\overline{\Delta R_C}$ be the resistance variation of the cell, while φ is changed by $\overline{\Delta\varphi}$ as in the figures. Since the experiment is a blank experiment ΔR_W is equal to 0 and we have that $\overline{\Delta R_C} \; < \; \tilde{\Delta R}_C$ in (14) when ΔR_W is put equal to 0 in this formula. In set-up II $R_W \simeq 10^{-1}\ \Omega$, and since Σ in the formulas of the circuit analysis is 3.3 Ω, one will find that even if the solution has e.g. an electric conductivity ten times higher than that of the previously considered KCl solution - which corresponds to a ten times higher f-value - $\overline{\Delta R_C}$ is still < about $1.4 \cdot 10^{-2}\ \Omega$, i.e. < about 4 o/oo of Σ. The condition for using the formula of the circuit analysis (42a) in [2] to establish the interdependence between $\overline{\Delta\varphi}$ and $\overline{\Delta R_C}$ is therefore in any circumstances approximately fulfilled. We thus have

$$\overline{\Delta\varphi} \simeq I_o \frac{R_4}{\Sigma} \overline{\Delta R_C} \; . \qquad (17)$$

Is e.g. $I_o = 3.3$ A and if it is borne in mind that $R_4 = 2\ \Omega$, one finds with the stated order of magnitude for $\overline{\Delta\varphi}$

$$\overline{\Delta R_C} \; < \; 5 \cdot 10^{-5} \; \frac{3.3}{3.3} \cdot \frac{1}{2} = 2.5 \cdot 10^{-5} \; \Omega \; .$$

When the curve has become parallel with the t-axis, we have $\xi = 0$. At the point of the φ-axis where the curved part of the diagram begins, we have $\xi = \xi_o$. Therefore, according to (13)

$$\overline{\Delta R_C} = \frac{\xi_o}{1+\xi_o} R_W^o < 2.5 \cdot 10^{-5} \ \Omega ,$$

from which, since $R_W^o = 10^{-1} \ \Omega$

$$\xi_o < 2.5 \cdot 10^{-4} . \qquad (18)$$

The limit given for ξ_o in (18) is very ample; because, as said, $\overline{\Delta\varphi}$ was often found to be ten times lower than the value used. From the experiments it cannot be inferred if the small "irregularity" of the diagram between $t = 0$ and $t = \bar{\tau}$ is due to chemical processes or if it represents the expiry of "non-faradayan" pulses. It may also be due to other causes. Thus dielectric polarization is ignored in the theory, but the water molecules in the electrolyte must after all orient themselves. An investigation of this can be made by performing a normal blank experiment with pure water, that is what might be called 'a blank experiment for the blank experiments'. At such experiments small irregularities were also found; however, they were so small that the irregularities in the electrolyte blank experiments must probably be ascribed to other causes than dielectric polarization.

The extremely small value of ξ_o and the value of $\bar{\tau}$ show that - at any rate in the cases investigated in the modified apparatus - the current pulses begin as extremely fast "non-faradayan" ones. This "ideal" and nearly instantaneous passing off is then succeeded by small delaying effects that fade out after $\frac{1}{2}$ second or less. After that period there is balance between the applied voltage and the counter-electromotive force in the remaining part of the measurement period.

On the above the following comments may be made, however. No experimental proof has been mentioned to the effect that one actually has $p = 0$ ($\xi = 0$) for $t > \bar{\tau}$, and not only $p = \text{const.}$, which would correspond to $i_L = \text{const.}$ *) for $t > \bar{\tau}$. In principle it is obvious how such an experimental proof can be given: before the filling of electrolyte into the cell, the set-up is so adjusted that $\varphi = 0$ (no deflection of the recorder) at balance in the bridge with the wire alone. Of the curves in fig. 8 the very specimen coinciding with the t axis for $t > \bar{\tau}$ must then appear. However, the set-up used does not lend

*) i_L is as before the current in the liquid.

itself to this demonstration because the adjustment of R_2 cannot be made accurately enough. To presume that b, respectively ξ, is considerably different from zero for $t > \bar{\tau}$ would, however, be contrary to the experiences with other set-ups used for other purposes and often described in the elementary literature, as it is a constant presumption in this section that operations are performed below the critical voltage δ for permanent electrolysis (the decomposition voltage).

Now the importance of the two previously mentioned complications for the modified apparatus must be examined.

1) The complication $R_C \neq R_W$ becomes insignificant. For $t > \bar{\tau}$, R_C is exactly = R_W and for $0 < t < \bar{\tau}$, we have $R_C = R_W$ in less than about 0.3 o/oo. This is seen from (12), $\xi < \xi_o$ and (18). R_W is thus recorded correctly through R_C in the whole of the t interval after the non-faradayan pulse is over, and chemical processes may begin to interfere. This stage is reached practically instantaneously. Let us in the following say that it happens at $t = 0_+$. In deriving the formula (65) in [2] for λ expressed by measured quantities, one should now everywhere by 'the initial value' merely understand the value at $t = 0_+$, which means that R_C^o must be replaced by $R_C^{0_+}$, i.e. by R_W^o because the wire does not become hot instantaneously.

2) The complication consisting in the fact that the simple linear relation of the circuit analysis between the recorder voltage φ and ΔR_C is not valid exactly becomes also insignificant. In (17) the symbol '$\simeq$' was used instead of the symbol '=', because when (17) was derived, the order of magnitude of ξ (or of $\xi_o = \xi_{0_+}$) was not known. Now when it has been found, it is seen from (12a) that $\Delta R_C = \Delta R_W$ during the whole experiment with a margin smaller than 0.3 o/oo + a contribution which is

$$< \frac{\xi_o}{1+\xi_o} R_W^o < 3 \cdot 10^{-4} \cdot 0.1\ \Omega \quad .$$

The presumption for the simple formula

$$\varphi = I_o \frac{R_4}{\Sigma} \Delta R_C$$

from the circuit analysis in [2], viz. that $\Delta R_C \ll \Sigma$ is then fulfilled just as well as for non-electrolytes in the interval $0_+ < t <$ the time for the expiry of the measurement period; because at the latter time, ΔR_W is chosen to be of the same order of magnitude as that applying

in non-electrolyte experiments. That this has been achieved may be seen from the recorder's deflection at the termination of the measurement.

It must now be considered established that set-up II could actually be used for the determinations performed with it in this work. That the modification, i. e. the transition from set-up I to set-up II, is necessary can easily be seen from the following example:

With set-up I it was found through blank experiments where I_o = 0.21 A that $\overline{\Delta\varphi} \simeq 2 \cdot 10^{-2}$ volts, which could only be registered by reducing the recorder sensitivity ten times. Since $R_W^o \simeq 16\ \Omega$ in I and $\Sigma \simeq 52\ \Omega$ one finds by using the by now slightly less good approximation (17):

$$2 \cdot 10^{-2} \simeq 0.2 \cdot \frac{10}{52} \overline{\Delta R_C}\ , \quad \text{i. e.} \quad \overline{\Delta R_C} \simeq 0.5\ \Omega\ .$$

One should then expect analogous circumstances to those described on page 21, where $\widetilde{\Delta R_C}$ instead of $\overline{\Delta R_C}$ was considered. In other words one must expect that ΔR_W is negligible compared to the contribution to ΔR_C from variation of p and that it cannot be separated from the latter. In the section on the experiments this is confirmed (see fig. 11 page 48).

From what is said in this section, it is seen that a low value of $f = \frac{R_W}{R_L}$ (R_L = the resistance of the liquid column) is advantageous so that the large cross section of the cell used can profitably be diminished. However, Alas [1] measures on electrolytic solutions using a considerably smaller cross section, but nevertheless he has to insulate the hot wire electrically. The "classical" set-up will not be practicable if modified only by diminishing the cross sectional area of the cell.

IV. On the Modification

In the preceding section it has been a constant assumption that experiments are performed below the decomposition voltage, δ, of the electrolyte. We shall now add some remarks on this point.

When treating electrolytic polarization phenomena in an electrolysis system Brønsted [3], page 405, uses $ZnBr_2$ as an example. He states the decomposition voltage of this salt to be the difference between the standard potentials of Zn and Br. This gives 1.8 volts (at approx. 20°C). The calculation seems to lean on the electrodes making up 2 half elements with $Zn^{++} + 2\theta \rightleftharpoons Zn$ and $2\,Br^- \rightleftharpoons Br_2 + 2\theta$ as active redox processes, θ being the electron, and further on that diffusion through the solution from these half elements can be ignored. This last-mentioned assumption is of course not strictly correct in the long run, and therefore it was also stressed earlier that stable thermodynamic equilibrium is not established in the cells, although the applied voltage is below δ. Actually the result will only be a very nearly fulfilled partial equilibrium, and it would therefore not be quite correct to use the formula of electro-chemical equilibrium thermodynamics for the electrode potential on the phenomenon, but it can probably give a certain indication.

For the sake of simplicity, let us consider an electrolytic solution in which we have only the ions ϕ^+ and χ^-, and let them be monovalent (i. e. ϕ and χ neutral). Further it is assumed that secondary processes do not occur at the electrodes so that the cathode process is only

$$\phi^+ + \theta \rightleftharpoons \phi \qquad \text{(a)}$$

and the anode process only

$$\chi^- \rightleftharpoons \chi + \theta\,. \qquad \text{(b)}$$

The 2 electrode potentials, $\mathcal{E}_1$ at the cathode and $\mathcal{E}_2$ at the anode, may then according to the mentioned formula be written as

$$\mathcal{E}_1 = E_o^1 + \frac{RT}{F} \ln \frac{a_{\phi^+}}{a_\phi}$$

$$\mathcal{E}_2 = E_o^2 + \frac{RT}{F} \ln \frac{a_\chi}{a_{\chi^-}}\,,$$

where

E_o^1 = standard potential of the (a) system

E_o^2 = standard potential of the (b) system

R = the gas constant = 8.315 J $^oC^{-1}$ $mole^{-1}$

T = absolute temperature

F = 96487 coulombs

a_x = activity for component x in the solution.

When the applied voltage is increased, the decomposition voltage is reached when χ and ϕ begin to appear in new phases, i.e. when $a_\phi = a_\chi = 1$. By subtraction of the corresponding $\mathcal{E}_1$ and $\mathcal{E}_2$ values we therefore find

$$\delta = E_o^2 - E_o^1 + \frac{RT}{F} \ln \frac{a_{\chi^-}}{a_{\phi^+}} .$$

In this formula the 'a''s mean activities in the layers saturated with ϕ and χ round the electrodes from which diffusion into the bulk solution is assumed not to occur. If the a's could be identified with the a's in the bulk solution, we would have $a_{\chi^-} \simeq a_{\phi^+}$ owing to the condition of electroneutrality. We would then have

$$\delta = E_o^2 - E_o^1 .$$

The validity of this formula and its use on more complicated electrolytic systems should actually be investigated a little more closely. The approx. 1.8 volts calculated to be the decomposition voltage for aqueous $ZnBr_2$ solutions are, however confirmed experimentally, and we shall assume that by means of the formula and tables of standard potentials it will be possible to obtain a reasonable idea of the maximal cell voltage for covering a fairly comprehensive range of electrolytic solutions.

Theoretically we may imagine an electrolytic solution with an arbitrarily low decomposition voltage; but if operations can be achieved with cell voltages of a few tenths of volts, a quite considerable range would seem to have been covered. In many - if not in most - cases further "overvoltage" phenomena will increase the difference between cell voltage and the voltage of actual decomposition. A cell voltage as that mentioned is just what has been obtained by the modification as the "classical" 16 Ω

wire*) with a diameter of 30-40 μm has been replaced by a wire of 0.1 Ω - and with a diameter of 500 μm -. This results in that instead of letting 0.1-0.15 A flow through the wire, it is necessary to feed 3.5-3.8 A to the bridge, of which 10/11 go through the wire, in order to obtain suitable recorder deflections.

The high current demands special precautions concerning the battery and its operation. Its capacity must be very high, and therefore five 12 volt accumulators in parallel were used. This will be mentioned in the subsequent section on the experiments. Suffice it to say here that it was possible to fulfil the demands on the battery.

The fact that the modified method cannot be used for measurements on extremely easily decomposable electrolytes may be considered a shortcoming. On the other hand, blank experiments give the necessary control so that it can be ascertained whether the method can be used in an actual case, and the control is easily made. There are, moreover, as earlier mentioned, advantages in using the method without electric insulation of the wire. Thus Alas [1] did not succeed in finding an insulation material that made it possible to measure on bases, whereas the blank experiments in the present work were successful with NaOH of the normalities 0.5, 1, 1.5, 2, and all through to the highest possible, approx. 20. From Alas's work it further appears that he has had practical difficulties with the insulation whose tightness must constantly be controlled.

In principle the electric insulation moreover involves a theoretical problem, which is most apparent if the insulation layer is imagined fairly thick. During the measurement period the flow of heat does not reach very far out radially from the wire. A great part of the conduction phenomenon therefore occurs in the insulation layer, and, roughly, what is determined may easily be the λ value of the insulation.

Expressed more exactly: we now have 3 phases, namely wire, insulation layer, and liquid, and the theoretical problem now becomes an intricate jump value problem that also involves the ρ, c, and λ values**) of the insulation material and its exact thickness which must be constant in the axial direction. Alas has avoided this problem, using a very thin layer of insulation. If the thermal resistance of the layer can be considered as

---

*) *Cf.* footnote page 21

**) As earlier 'ρ' and 'c' designate density and specific heat.

surface distributed in the surface of the wire, it can be demonstrated that the simple, i. e. the uncorrected, theory that corresponds to a line source for the heat, leads to an unchanged expression for λ. But for extremely thin layers - perhaps almost monomolecular ones - even the slightest solubility in the electrolytic solutions must presumably become fatal.

Finally should be mentioned the conceivable possibility of changing to use alternating current and thus eliminating the polarization instead of exploiting it as done here. The author has not seen this possibility mentioned in the literature, and it also seems to be little attractive. If it is to be of any importance, the idea must be that it would be possible to operate at "high" voltages in a "classical" set-up with a thin wire. However, in that case a considerable fraction of the electric current will run in the liquid during the entire measurement period (cf. $f = R_W/R_L = 4$ found in the preceding section for set-up No. I with 1N KCl solution). It will thus be very doubtful whether the heat production in the liquid can be controlled, i. e. whether it can be corrected for, as the production will not be homogeneously distributed but more dense round the wire retainers than round the centre of the wire. Furthermore a reliable correction must be worked out for the fact that the difference between R_C and R_W will now be very pronounced.

V. The Experiments

a). General Remarks

The experimental work proper was excellently done by P. Mørk Christensen who also contributed original suggestions for improvements of the apparatus and organized the computer processing.

The measuring cell is shown in fig. 9 with all dimensions in mm, and the figure gives most of the necessary information about this part of the apparatus. The radius of the wire was measured to be 0.500 ± 0.001 mm. (It will appear from the following that its value is of minor importance as, within certain limits, a systematic error in the value does not play any part on account of the iterative method of calculation). The initial state of the liquid in the cell must be temperature homogeneous. At the beginning of the experiments the temperature homogeneity was checked on 3 resistance thermometers placed at different levels immediately outside the cell which, in its turn, was placed in a thermostat. With the resistance thermometers temperatures could be determined with an accuracy of $\pm 0.02^{\circ}C$.

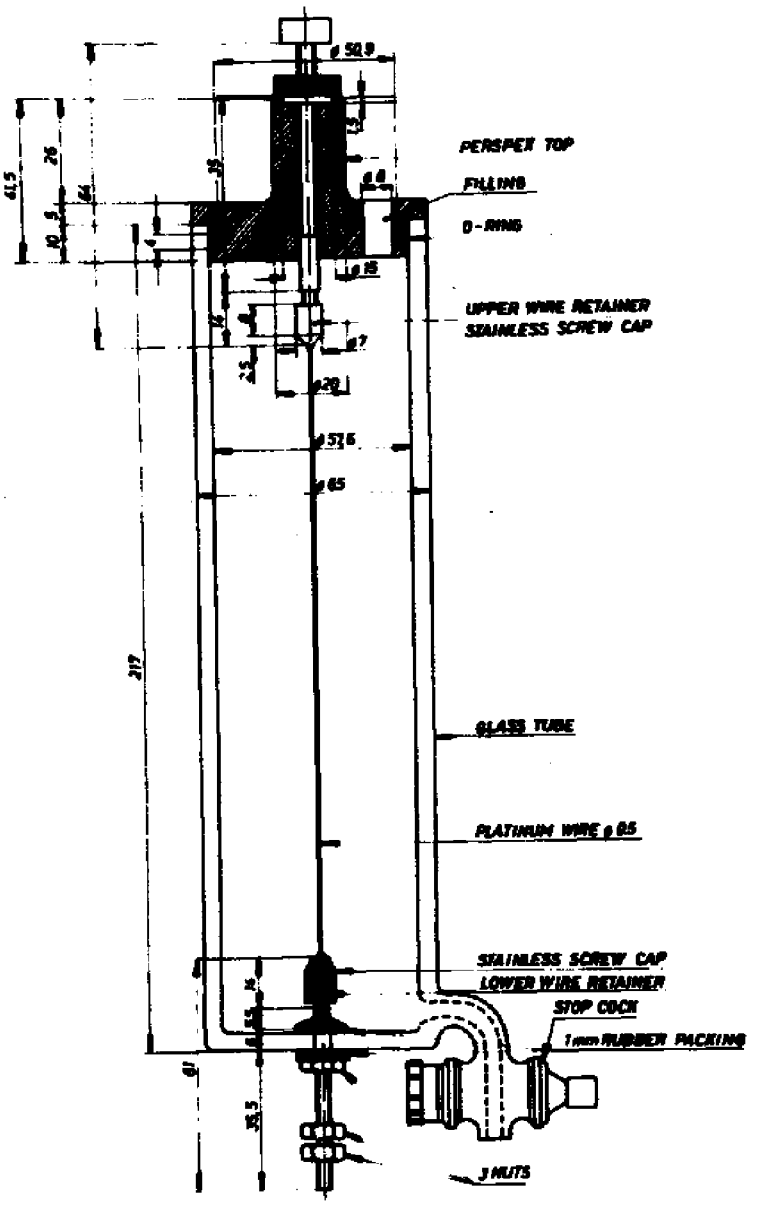

PERSPEX TOP
FILLING
O-RING
UPPER WIRE RETAINER
STAINLESS SCREW CAP
GLASS TUBE
PLATINUM WIRE ø 05
STAINLESS SCREW CAP
LOWER WIRE RETAINER
STOP COCK
1mm RUBBER PACKING
3 NUTS

Fig.9

Between the individual experiments the cell was at rest for a suitable time. For reasons of convenience a water thermostat with redistilled water was used, and the electrical conductivity of the water was checked from time to time. Besides, the cell was only submerged in the thermostat water as far as nearly to the upper end of the perspex "top" shown in fig. 9. Thus the current was supplied outside the thermostat water through a wire soldered on the upper round nut. The cell was placed in the thermostat on a three-legged, stainless-steel disc, the legs of which were adjustable so that the wire could be placed vertically, sighting in 2 directions perpendicular to each other after a plumb line. The circuit in which the cell was built in is shown schematically on page 19, figs. 3 and 4, with greatly rounded values for the resistances. As will be mentioned in the following, currents of 3.5-3.8 A and measuring periods of 8-10 seconds were found to give the best results. An ordinary accumulator was therefore not sufficient as the source of current, E fig. 3. The circuit analysis presupposes (cf. [2], page 44) that the variation of the terminal voltage during the measurement period is extremely small. Further the battery should not be greatly discharged after a reasonably comprehensive series of measurements. Consequently five 12 volt accumulators were used in parallel, which gave a considerable battery capacity, but even this was not enough to satisfy the demand on the constancy of the terminal voltage mentioned in [2], page 44.

The ammeter, fig. 3, generally clearly showed a drop in current during the experiments which could not be explained by the resistance change of the cell.

Upon the advice of Arne Jensen an extra circuit - not shown in fig. 3 - was built in through which the battery could for some time before the beginning of the experiments be discharged at the same current as the one that was used at the subsequent measurements. By a direct switch from such a discharge to measurement the desired result was obtained, which Arne Jensen indicated by means of oscillographic recordings. Later L. Palgaard of the Electronics Department, Risø, confirmed by means of very accurate measuring equipment that by using such a preparatory discharge in a suitable way it is actually possible to fulfil the condition mentioned in [2], page 44, namely that the terminal voltage changes by less than 10^{-2}% during an experiment. (Palgaard has written an internal note about his measurements).

The components of the bridge were assembled with extremely thick copper rods and copper wires, and it was carefully analysed for contact resistances

or components that might be heated appreciably during the experiments and thus falsify the recorder registrations. For this purpose were used experiments of the kind called 'blank experiments for the blank experiments' or 'blank experiments with pure water', on page 27. After a number of alterations of the original set-up the result was that, apart from the "small irregularities" also mentioned on page 27, the recorder diagrams in such experiments*) were absolutely parallel with the time axis or rather with the line that the recorder draws "without signal" (the paper might be slightly askew).

As mentioned, the values of R_3 and R_4 in fig. 4 are greatly rounded. The 2 resistances were manganin helices fastened to very thick and short copper rods to which also the other bridge components were connected. With a Müller bridge they were measured quite accurately to be

$$R_4 = 2.8125\ \Omega; \quad R_3 = 0.2239\ \Omega \text{ at } 20.00^{\circ}C,$$

and their temperature was kept constant by immersion in redistilled H_2O. As the copper rods were practically without resistance, there was no problem of supply resistances to R_3 and R_4. The same applied to the variable resistance, R_2, which consisted of a precision resistance box on which the resistance could be read with 2 decimals. It had its terminals directly connected to the copper rods, and through quite short and thick copper wires it was shunted with a similar box for fine adjustment at the balance adjustment to be mentioned shortly. Strictly speaking it should be possible to read R_2 with 3 decimals as its value is approx. 1 Ω. The mentioned resistance boxes were originally components in a "classical" set-up for measurement on organic reactor coolants, where the value of R_2 was approx. 10 Ω. The standard deviation of λ is calculated directly on the computer on the basis of 10 determinations, and as this proved to give a satisfactory value, the boxes were retained in the modified set-up for measurement on electrolytic solutions. The standard deviation was generally about 1.5% (often better), i.e. the mean of 10 determinations can be given with the accuracy of $\pm$ 0.5% or less. If this is to be further improved, it must presumably be possible to measure R_2 more accurately.

---

*) i.e., experiments in which the Pt-wire had been replaced by a manganin wire.

As [2] forms the basis of the present report, we shall in the following refer directly to [2] without repeating formulas or the meaning of symbols in detail.

In formulas (67) and (69) in [2], pages 59 and 60, it is apparent that 'Σ' means the sum of all bridge resistances inclusive of supply resistances. According to the above only the cell resistance has a not-negligible supply resistance when, as in the circuit analysis in [2], cell resistance is put = wire resistance (or when (12), page 20, is used for electrolytes). The value of cell resistance + supply resistance was found by balancing with H_2O in the cell, and the determination was repeated every time the cell had been taken apart for cleaning.

The wire resistance proper is only of interest for the control of "the level" mentioned in [2], page 60, i.e. for calculation of C by (70) in [2], as its value, as shown on page 59 in [2], is reduced out at relative measurements.

The wire resistance was measured with a Müller bridge by fitting up of a piece of wire between very thick copper blocks. The result was 0.5439 $\Omega\ m^{-1}$ at 20.00°C. As the length of the wire between the retainers in the cell was constantly 167.3 mm, this corresponds to

$$R_W = 0.0910\ \Omega \quad \text{at } 20.00^{\circ}C.$$

As will be understood from the exposition of the method of calculation in [2], an accurate balancing adjustment before recording of diagrams is unnecessary. The diagrams may, as mentioned in connection with fig. 12, page 55 in [2], be differently displaced on the paper. To obtain a reasonable position a coarse balancing was performed with short pulses of current at full measuring current and the recorder pen as indicator.

The treatment of the recorder diagrams must now be explained in more detail than has been done in [2], section VI. As mentioned in section I, page 7, and in [2], corresponding time and voltage values have been measured manually, and the code has been adapted for these pairs of values to be read into the computer. The question is, however, what parts of the diagrams pairs of value can be taken from. At the lower end the parts are at any rate limited by the condition mentioned in [2], page 58, namely $x = 4\varkappa t/r_o^2 \geq 5$ ($\varkappa$ is the thermometric conductivity of the liquid, r_o is the radius of the wire). At the upper end the parts are limited by turbulence disturbances. Further the entire method of calculation of λ in [2] builds upon the

power variation in the wire and the final length of the wire not giving rise to any errors. The 2 sources of error originating from the fact that this is idealizations have loosely been treated in [2], pages 47-52, with reference to a more detailed discussion in the present report. This discussion will be given now.

With the designations*) used in [2], formula (64) of [2] is

$$\lambda = \frac{q_o \alpha}{4\pi\phi},$$

where q_o is the constant q-value presupposed in this formula. On page 47 of [2] it was, however, found that q varies by less than 1% during the measurement period, and that during that period it is monotone non-decreasing. Calculating with the initial value q_o in the formula cannot therefore - at relative measurements - cause any essential error. The error must be of the order of a few o/oo. However, ϕ means the slope of the asymptote in a φ versus lnt-diagram such as fig. 13, page 56 of [2]. The asymptote is, as shown in the mentioned figure, generated by subtraction of the segments K from the φ-curve if q is constant. As q varies during the experiments, K is not subtracted from the quite correct curve, φ^*, if in the recorder diagram φ is not corrected, but from the incorrect recorder diagram. Thus strictly speaking a straight line does not result; but the computer treats the recorded set of points according to the least-squares method as if it was part of a straight line. On page 51 of [2] it was found that φ differs by less than 1% from φ^*. If, instead of using the recorder diagrams from the t-value corresponding to $x = 4\pi t/r_o^2 = 5$ (i.e. approx. $\frac{1}{2}$ second), more of them is removed at the lower end (e.g. the parts corresponding to the first approx. 1.5 s), the curved φ-diagrams are very close to the asymptotes. Moreover all the φ-values are then comparatively high, and 1% of $\varphi^* \simeq$ 1% of φ.

Without complicated calculations with the formulas on pages 48-51 of [2] it can therefore be estimated that only an error of $\lesssim$ 1-2% is made on the slope ϕ by the procedure just outlined. At measurements relative to H_2O only a small error will therefore occur from ϕ even though the elec-

---

*) q, (q_o) is the power per unit length of the wire, α is a constant during a measurement determined by the current from the battery and the resistances in the bridge, and ϕ is the slope of the asymptote of the recorder voltage versus lnt diagram.

trolytic solutions are rather concentrated and not as presupposed in [2], page 52, very diluted.

Then only the effect of the final length of the wire remains among the complications. The problem that arises in this connection is, as shown in [2], page 25, theoretically very intricate. During the experiments the effect - or perhaps rather: this effect + the effect of the q-variation - has, however, manifested itself in a quite simple way:

Let us consider a measurement on an arbitrary electrolytic solution. The measurement period may be for instance 10 seconds. At successive calculations of the λ-value of the solution parts of the recorder diagram corresponding to shorter and shorter time intervals are now used, values being cut from the upper end of the diagram. By so doing constantly decreasing values for λ are found if a fixed value for the quantity *) $C^*_{H_2O}$ (see page 59, of [2]) is read into the computer. Altogether the decrease in the λ-value may be about 2-3% before there are too few points left for the standard deviation to become reasonable.

In experiments with H_2O - which is the chosen basis substance at the relative measurements - it is found, however, that the value of λ_{H_2O} determined by the same procedure decreases correspondingly. At each way of cutting the $C^*_{H_2O}$ read in may be adjusted so that λ_{H_2O} becomes correct. The λ-value of the electrolyte then becomes constant within a few o/oo when values for $C^*_{H_2O}$ corresponding to the same way of cutting of the H_2O-diagram as of the electrolyte diagram, are used. In other words, the condition of keeping the interval of the measurement period fixed during the experiments both on water and on electrolytic solutions must be observed rather strictly. This corresponds to the quantity γ mentioned page 26 of [2] being dependent on t.

If there were no complications from the final length of the wire (and from q-variation), the said condition would be irrelevant. Observance of the condition gives, as mentioned, a fixed λ-value for the electrolyte, i. e. a value independent, within certain limits, of the way of cutting. As will be seen in subsection b), the result agrees well with the literature values for aqueous solutions of NaCl, KBr, and $CuSO_4$, each in the concentrations 0.5, 1, 1.5, and 2 N. This must be said to be decisive evidence that the

---

*) $C^*_{H_2O}$ is a quantity introduced in [2] and has the property that the thermal conductivity of the liquid, λ, can be calculated from an expression of the form $\lambda = \lambda_{H_2O}/C^*_{H_2O}$ · a factor containing only measured quantities.

final length of the wire (and q-variation) can be ignored when the procedure is correct *) even when measurements are made on rather concentrated electrolytic solutions relatively to H_2O.

As for "the fixed interval of the measurement period" it was in all cases put at about 1.6 s $<$ t $<$ 8 s. With a current of 3.5-3.8 A was then obtained an ample number of points and a correspondingly small standard deviation. When the recorder diagrams were transformed to a logarithmic time scale, the "change of direction" mentioned in [2], page 27, was found to occur later than after the 8 seconds. This indicates that turbulence has either not occurred during the measurement period or that it has only occurred outside the narrow zone within which the thermal conduction is (practically) confined **). (Near the cell walls there may have been vortices in the upper and the lower part of the cell, but apparently such vortices have not disturbed the measurement if they have been present). Lower values for the upper limit of the measurement period gave as mentioned above the same λ-value by the "correct" procedure, but if the time was below 4-5 seconds, the standard deviation increased quite considerably. As the λ measured was thus not changed with a shorter measurement period within certain limits, the conclusion must be that the approx. 8 seconds have been "safe" as far as turbulence disturbances are concerned. With a view to the number of points approx. 8 seconds are, moreover, as mentioned, suitable at the chosen currents.

A number of experiments were also made with different currents flowing to the bridge. At currents below 2.5 A the diagrams became very small, and the sets of points were consequently so small that the standard deviation became poor. As for the interval of the measurement period it is also a condition (cf. [2], page 26) that the wire power, and thus the current, I, must be fixed at the relative measurements. If this condition is not observed, λ-values for the same electrolyte varying by 1-2% were found in the interval 2.5 A $<$ I $<$ 3.8 A.

---

*) i. e. when the procedure is in accordance with what has been said immediately above.

**) Cf. [2], page 17.

In this section there may finally be reason to mention that the cutting of the lower end of the diagrams mentioned above is in good agreement with the most favourable conditions for the iteration process which, according to [2], section VI, leads to λ. What is to be found iteratively is the corrections, K, fig. 13, page 56 of [2], at given times. K would of course be useless if it did not correspond to a known value of t. Let us first assume that the density, ρ, and specific heat, c, of the liquid are known without any error.

According to [2], K is at the time t found by intermediate change to what was called in [2] 'a fig. 5 a-curve' *). On the latter a segment, K^*, and an $x = 4\varkappa t/r_o^2$ correspond to K and t respectively. But when at the beginning of the iteration λ and thus also $\varkappa$ are only known within a certain margin of error, $\varkappa$ for instance as $\varkappa + \frac{p\varkappa}{100}$, a K^* at a wrong x-value, which we may call 'x^*', will be chosen in the "fig. 5 a-diagram"! Further it is seen that $\ln. x - \ln. x^* = \Delta$ is constant, namely determined by p. If Δ is small - i. e. p is small - the segment that is wanted is

$$K^*(x) = K^*(x^*) + \frac{dK^*}{dx}\,\Delta x = K^*(x^*) + \frac{dK^*}{d\ln. x}\,\Delta ,$$

i. e. it is not = $K^*(x^*)$, which is what is found. It is, however, quite elementary to see that if the curved fig. 5 a-diagram has become practically straight, $dK^*/d\ln. x$ becomes practically constant. As Δ is constant, as has been mentioned, we thus find K^* + const. and not the K^* sought.

As now K^* is to be converted "back to fig. 13 in [2] from fig. 5a in [2]" to correct the voltage curve, K^* must be multiplied by the factor $\frac{q\alpha}{4\varkappa\lambda}$, where α is given by (56), page 47 in [2] **). As at the beginning of the iteration λ is known approximately as $\lambda + \frac{p\lambda}{100}$, we thus have as a result of the correction

$$K' = \frac{q\alpha}{4\varkappa\lambda\,(1 + \frac{p}{100})}\,\{\,K^* + \text{const.}\,\}$$

---

*) This curve is fixed through ρ and c. The family of "fig. 5 a-curves" are sketched in [2], page 29. The coordinates of the family are dimensionless, namely $\frac{4\varkappa\lambda T_W}{q}$ and $\ln(4\varkappa t/r_o^2)$, where T_W = the temperature of the wire.

**) α is defined in [2], equation (57), as the ratio of recorder voltage to wire temperature.

and not, as desired,

$$K = \frac{aq}{4\pi\lambda} K^* \quad .$$

It will be seen that (if p is small), we have

$$K'-K = -\frac{aq}{4\pi\lambda} \frac{p}{100} K^* + \text{const.} \qquad (19)$$

In (19) the constant term, 'const.', is, however, of no importance as only the slope of the asymptote in the "fig. 13-diagram" in [2] is sought. It is therefore irrelevant whether at each iteration step the corrected curve is displaced by a constant distance in the direction of the φ-axis. The operations may therefore be performed as if we had

$$K = K' + \frac{aq}{4\pi\lambda} \frac{p}{100} K^* \quad . \qquad (19a)$$

Looking at the enlargements of the "fig. 5 a-curves" of the literature mentioned on page 58 of [2], we find that we must have $t > 1.5\text{-}2$ s in order that the family of curves may be said to have become straight lines with a reasonable approximation when the value of $\varkappa$ is about equal to the value of $\varkappa_{H_2O}$ (which is the case with the electrolytic solutions investigated).

By using only curve points corresponding to $t > 1.5\text{-}2$ s we thus achieve 1) that the foundation (19) for (19a) is valid, and 2) that the first inexact λ-value becomes reasonable, i.e. we get a reasonable start of the iteration. There is consequently reason to believe that the term with p in (19a) disappears fairly fast in the course of the iteration. If instead of the term 'const.' (19) contained a complicated term from the curvature of the curves at small t-values, the first iteration step might become very wrong, and the iteration process might (at best) become only very slowly converging and perhaps even diverging.

The above presupposes that ρ and c are known without errors. "Experiments" with altered ρ- and c-values read into the computer have, however, shown that the calculated λ-value is only slightly dependent on ρ and c (and thus on the curve parameter*) $\rho\, c/\rho_W c_W$). This means that it has been possible to take ρ- and c-values for the solutions relatively uncritically from the data literature or, in other words, that the experiments have not been dependent on the possibility of making accurate measurements

*) ρ_W and c_W are the ρ- and c-values respectively of the wire material.

of c and ρ. Generally it was found that a change in $\rho \cdot c$ of 10% in one direction resulted in a change of the calculated λ of 1-1.5% in the opposite direction.

In the above we imagined that the error in x at the beginning of the iteration was due to an error of $\varkappa$, and it was shown that this error would be iterated out if it is not too high. As $x = 4\varkappa t/r_0^2$, it will be seen that a small error on the wire radius r_0 is just as harmless as a small error on $\varkappa$, and that the wire radius must therefore not necessarily be known with the greatest possible accuracy.

(19a) can be written

$$K = K' + \frac{p}{100} K ,$$

i.e. after the first iteration step there is an error of p % in K. As K is to be subtracted from φ (cf. fig. 13 of [2]), we therefore after the first step find the φ-value

$$\varphi_1 = \varphi - K \left(1 - \frac{p}{100}\right) ,$$

while the value

$$\varphi_{as} = \varphi - K$$

is sought.

We now have

$$\varphi_{as} - \varphi_1 = -K \frac{p}{100}$$

from which

$$\frac{d\varphi_{as}}{d \ln t} - \frac{d\varphi_1}{d \ln t} = -\frac{p}{100} \frac{dK}{d \ln t} = -\frac{p}{100} \alpha \frac{q}{4\pi\lambda} \frac{dK^*}{d \ln t} ,$$

or according to (19c) and (57) both in [2]

$$\frac{d\varphi_{as}}{d \ln t} - \frac{d\varphi_1}{d \ln t} = -\frac{d\varphi_{as}}{d \ln t} \cdot \frac{p}{100} \frac{dK^*}{d \ln t} .$$

The error expressed in percentages in the slope $\frac{d\varphi_1}{d \ln t}$ compared with the desired slope of the asymptote $d\varphi_{as}/d \ln t = \Delta\varphi_{as}/\Delta \ln t$ is thus

$$p \frac{dK^*}{d \ln t} .$$

From the enlargements of the "literature diagrams" mentioned in [2] page 58 we estimate

$$-\frac{dk^*}{d \ln t} \simeq 0.2$$

for $t \simeq 1.5$ s.

The error in per cent on λ resulting from errors of $\Delta\varphi_{as}$ / $\Delta \ln t$ will thus at each step be multiplied by approx. 0.2.

The course of the iterations was found to be in agreement with the above: 2 or 3 iterations were sufficient as the first λ-value might be for instance 7% too high.

b). Results of the Experiments

1. Determination of the Quantity $C^*_{H_2O}$ Defined in [2], page 59

According to the description of the calculation method in [2], section VI, the value of $C^*_{H_2O}$ in formula *) (69) of [2] must be determined first and foremost. The current at which the λ-measurements on the electrolytic solutions are to be made and the fixed interval of measurement time being used for these measurements must also be used at this determination. It is made by filling of the cell with redistilled H_2O and recording of a diagram. A tracing of such a diagram reduced to half size is shown in fig. 10.

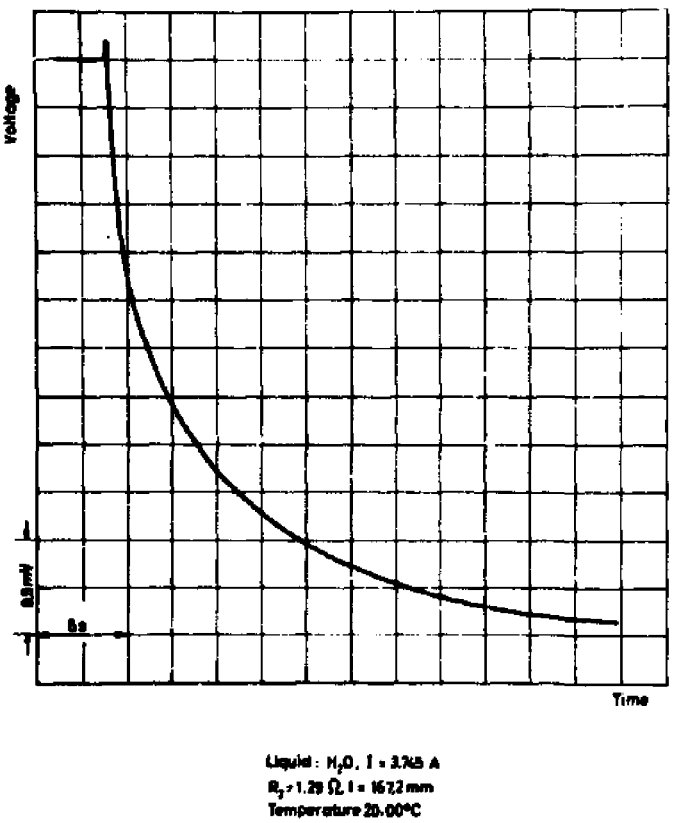


Fig. 10

l is the length of the wire and I the current from the battery. The curve in fig. 10 and all curves mentioned in the following refer to 20.00°C. On page 59 of [2] was introduced, in addition to $C^*_{H_2O}$, the quantity C which is a constant property of the apparatus

*) The formula has the form $\lambda/\lambda_{H_2O} = 1/C^*_{H_2O}$ · a function of quantities measured during the λ determination.

given by*) (70) of [2]. Its connection with $C^*_{H_2O}$ is that $\lambda_{H_2O} \cdot C = C^*_{H_2O}$.

From a diagram in Straumann [8] it is seen that at 20.00°C the measurements of λ_{H_2O} of various researchers group themselves evenly round the value

$$\lambda_{H_2O} = 6.00 \cdot 10^{-1} \ \frac{W}{m\,^oC} \ .$$

This value was therefore chosen as the most reasonable one for the basis substance H_2O. If C is now calculated according to (70) of [2], we have a "theoretical" value, $C^*_{theor.} = 6 \cdot 10^{-1} \cdot C$ in the MKSA-system for $C^*_{H_2O}$. As the latter is a fixed input value in the computer program, we may then proceed as follows: $C^*_{theor.}$ is read in for $C^*_{H_2O}$, and λ_{H_2O} is calculated as the arithmetical mean of 10 individual measurements. As, on account of the systematic errors, $C^*_{H_2O} = C^*_{theor.}$ cannot be quite correct, this does not give exactly $\lambda_{H_2O} = 6 \cdot 10^{-1}$ W/m °C. Formula (68) on page 59 of [2] shows, however, that the value found is inversely proportional to the $C^*_{H_2O}$-value used. It is therefore quite easy to "adjust the value of $C^*_{H_2O}$" so that the mean value for λ_{H_2O} is calculated by the computer to be exactly $6 \cdot 10^{-1}$ W/m °C. We may say that we have then "calibrated" the apparatus.

By this procedure it is evident that the relative standard deviation of $C^*_{H_2O}$ = the relative standard deviation found for the mean value of λ_{H_2O}.

In 2 series of 10 individual measurements each the computer gave the standard deviations 0.34% and 0.35%. The mean of the means of the series was

$$C^*_{H_2O} = 1.426 \cdot 10^4 \ W \ \Omega^{-3} \ ,$$

and the standard deviation of this is thus approx. 2.5 o/oo.

This deviation is so small that it is ignored in the program which simply gives the standard deviation of λ according to the usual formula for this quantity on the basis of the individual λ-values regardless of the fact that $C^*_{H_2O}$ is not a constant that is quite free from inaccuracy.

At the $C^*_{H_2O}$-determination I was $\sim$ 3.8 A, and the first points of the diagrams corresponding to 1.7 seconds had been cut away. Moreover the measurement period was as mentioned about 8 seconds. These conditions were observed in all the measurements on electrolytic solutions men-

---

*) This formula is given on page 46 of the present report.

tioned in the following.

According to (70) on page 60 of [2] we have with the designations used in [2]

$$C^{*}_{theor.} = \lambda_{H_2O} \cdot C = \lambda_{H_2O} \cdot \frac{4\pi l}{R_4 R_C^2 \beta_{corr.}} \quad .$$

In this formula $R_C = R_W$ = the wire resistance which is given on page 37, and l = the length of the wire was 167.2 or 167.3 mm in all experiments. R_4 is given on page 36. If $\beta_{corr.} \simeq \beta$ is put = $3.8 \cdot 10^{-3}\ ^{o}C^{-1}$, we find

$$C^{*}_{theor.} = 1.425 \cdot 10^{4}\ W\ \Omega^{-3} \quad .$$

This agrees extremely well with the mentioned, experimentally determined value; but it must be borne in mind that β is not measured (and corrected, cf. [2], section IV), but taken from the literature, and further that at different measurement periods and currents $C^{*}_{H_2O}$ may be found to deviate by a few per cent from the experimentally determined value (which, according to the above, page 39, does not mean that the λ found for the electrolytes varies. The procedure just has to be "correct"). The result must be said to show that "the level" - as it was called on page 60 of [2] - is reasonable.

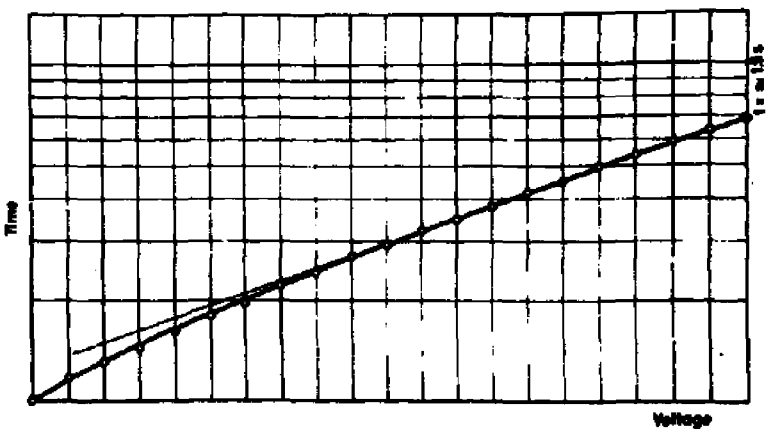


Fig.10a

In fig. 10 a the earliest part, and in fig. 10 b the latest part, of fig. 9 are shown transformed to logarithmic time scale. The figures are only intended as sketches as they were of greatest interest during the initial stages of this work. Now the computer performs the necessary transformations. The scales in the 2 figures are therefore irrelevant. Fig. 10 b, however, clearly shows the curve corresponding to turbulence disturbances when the measuring period is exceeded. The 2 tangents in the figures have been

drawn to set off the curvatures.

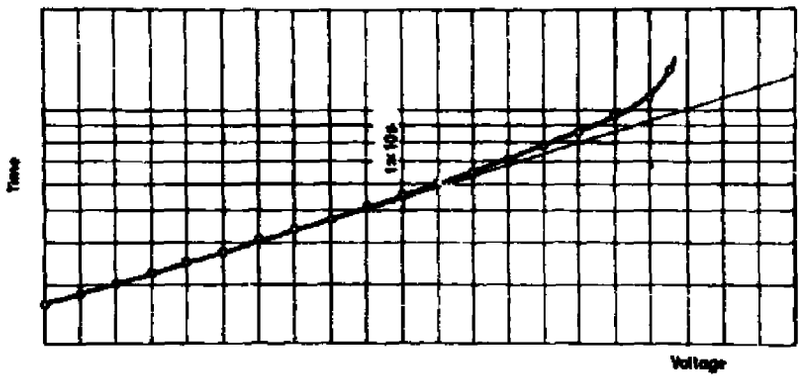


Fig. 10b

Fig. 10 b is remarkable in that the turbulence disturbances are clearly seen after about 10 seconds, but that phenomenon is not seen in fig. 10 itself. An example, where a change of direction can also be seen in the recorder diagram proper, is shown in fig. 13.

For all the electrolytic solutions investigated courses corresponding to figs.*) 10a and 10b are found after transformation to a logarithmic time scale.

Although the "classical" set-up for measurements on dielectric liquids has been greatly modified for measuring on electrolytes, the developed modification must of course also be usable for the former.

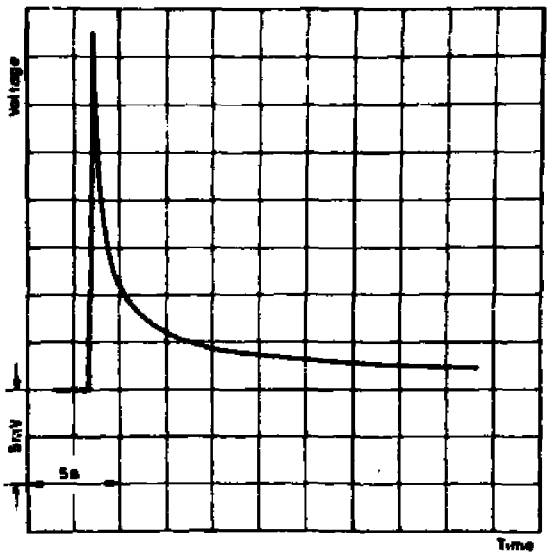
For all the electrolytic solutions investigated in the present work, it is easily calculated by using the tables later in this section that the condition $\rho\, c / \rho_W c_W \rangle 1$ for the validity of (66) on page 58 of [2] is fulfilled ('ρ' and 'c' mean density and specific heat respectively, and index 'W' means that the values are the values for the wire material, i.e. platinum). But for many organic liquids (such as e.g. ethyl alcohol, carbon tetrachloride) the said condition is not fulfilled. If measurements are to be made on such liquids **), the mentioned formula of [2] must be altered, i.e. other "extra terms" than those used in [2] must be worked out. That can also be done; but the present work has been limited to measurements on aqueous electrolytic solutions. Some quite roughly informative measurements were, however, made on ethyl alcohol, carbon tetrachloride, and glycerol relative to H_2O, the corrections K being left out, and the "straight" parts of the semilogarithmic diagrams between the initial and the final curvature being used directly. The results were within the intervals in which the corresponding values of various researchers are distributed.

---

*) As will appear from what was said above, these figures apply to H_2O.

**) In that case it may be better not to measure relative to H_2O.

2. Blank Experiments on Electrolytic Solutions with Manganin Wire as Described on Page 22 ff

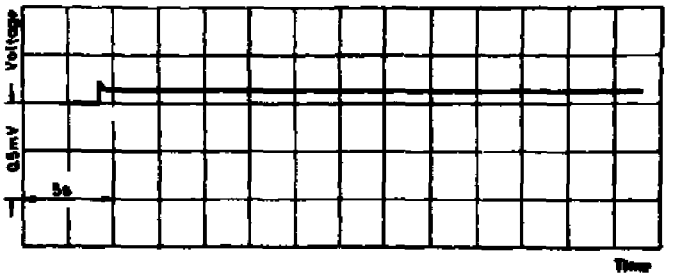


Blank experiment in "classical" set-up on 0.5N NaCl
I = 0.21A

Fig. 11

Fig. 11 shows a tracing, reduced to half size, of a recorder diagram chosen at random from blank experiments on an electrolytic solution in the unmodified, "classical" set-up. Its appearance is characteristic of all blank experiments on the electrolytic solutions used in this set-up whose bridge is in fig. 4 called 'bridge No. I'. The cell had a wire radius = r_o = 20 µm, and a wire length = l = 18.5 cm.

As an example of blank experiments in the modified set-up (r_o = 250 µm, l = 16.7 cm) is in fig. 12 shown a tracing - also reduced to half size - of such an experiment



Blank experiment in modified set-up on about 2N Na OH
I = 3.8 A

Fig. 12

on 2N NaOH. Also the course of this diagram is characteristic, only the small jump which on page 26 was called '$\overline{\Delta\varphi}$', was found generally even smaller. This applied to for instance blank experiments on the strongest possible NaOH-solutions, i.e. approx. 20 N ones.

Figs. 11 and 12 show that the recorder sensitivity in the "classical" set-up had to be reduced by 10 times as compared with the modified set-up for the curve to be recorded.

The same therefore also applies to attempts at direct measurements

on the electrolytic solutions in the classical set-up. This was also confirmed by experiments. It follows from the theory in section III that it would be unrealistic to regard diagrams from "measurement" in the classical set-up as superposition of blank curves and "true curves" so that the latter could be found by subtraction of the blank curves from the recorded curves. If this was possible, the "true" diagrams for electrolytic solutions would, moreover, have been obtained at one tenth of the sensitivity used for non-electrolytes. They would therefore for the same rise in temperature in the wire at the end of the experiment be so "small" that they could not be used.

From the theory in section III it further follows that the modified apparatus - which gives blank curves as in fig. 12 - may be used for measurements on electrolytes without any complications whatsoever. In principle measurements may therefore be made on e. g. the mentioned 20 N NaOH-solution. The only reason for not doing this is that the mechanical and thermal properties of such a solution are so different from those of H_2O that the author dared not assume that the systematic errors would be sufficiently small*) at measurement relative to H_2O. Thus a 20 N NaOH-solution is extremely viscous. If, on the other hand, the possibility mentioned in [2], pages 22 and 24, of improving this work - by insertion of potential wires and by building a slightly more complicated circuit - is implemented, measurements can be made on NaOH, KOH, and other ordinary bases in any concentration.

3. Measurements of λ-Values for Some Aqueous Electrolytic Solutions at Room Temperature

In the following the results of the measurements are given in tables and diagrams, and finally they are discussed.

All chemicals from which the aqueous solutions were made, were analytical reagents. The solutions were prepared and analysed**) by the Chemistry Department at Risø.

---

*) Cf. remarks in [2], page 26.

**) The last decimal in the given normalities is uncertain, but from the λ-dependencies of the normalities found it is seen that this is of no importance.

In the tables 'N' means the normality of the solutions (= their molarity, except for the $CuSO_4$-solutions whose molarity is $\frac{1}{2}$ N).

ρ and c are densities and specific heats given in the MKSA-system. 's' means standard deviation and 's_{10}' standard deviations for the mean of 10 measurements, both s and s_{10} being given as % of λ. All λ-values given are such means of 10 measurements.

The ρ- and c-values were found by means of the standard works Landolt-Börnstein, Physikalisch-Chemische Tabellen and Gmelin's Handbuch der anorganischen Chemie, and by means of Alas [1]. The last-mentioned work, however, contains no c-values, but only the ρ-values for the solutions of salts examined. Where necessary the concentration units used were converted into normality, and interpolation and extrapolation were used in the tables of the mentioned works. By comparisons, the values that seemed to be the most reliable were chosen.

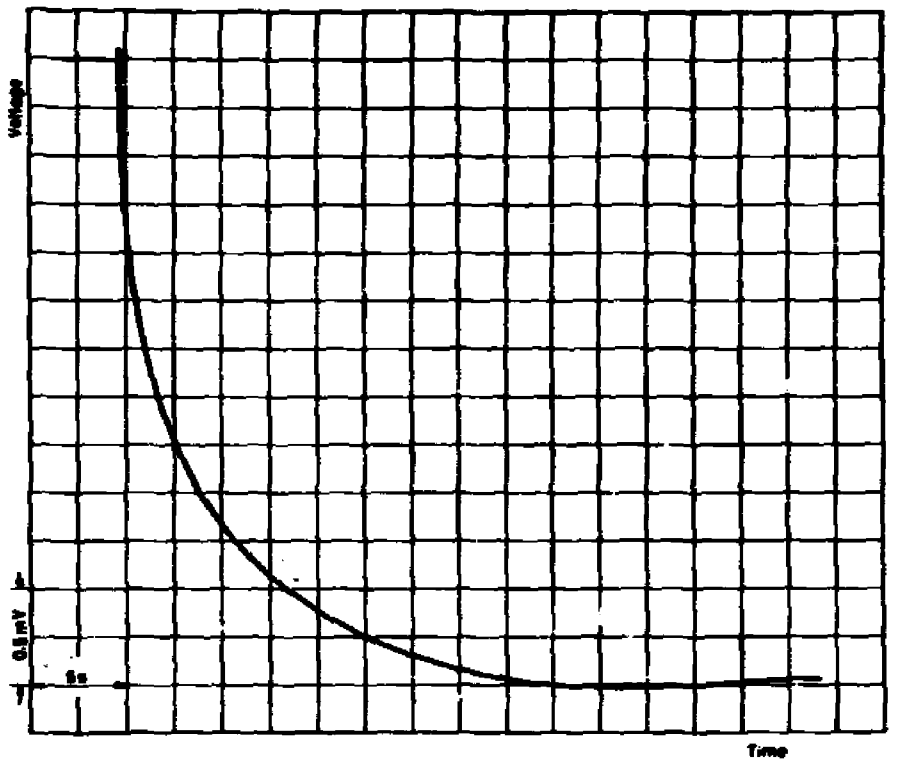
For the $CuSO_4$-solutions (table III) only rather inaccurate c-values were found as they are mean specific heats (originating from older works). The value for 2 N $CuSO_4$ is for instance the mean specific heat in the interval 15-49°C, and it is seen that it fits poorly with linear extrapolation from the others given. Linear extrapolation from the two preceding values *) would give the value 3406, which is approx. 4% less than that chosen. According to an earlier remark (page 43), the extrapolated value would reduce the chosen λ by 5-6 o/oo, but the figures do not indicate a linear connection between c and N, and the c-value used is therefore considered the safest. Altogether, and also in accordance with the earlier remark, ρ- and c-values must not necessarily be known very exactly, and - perhaps with exception of the values for the $CuSO_4$-solutions - the values given in tables I-V can be considered as more than sufficiently accurate.

A characteristic recorder diagram from the electrolyte experiments is shown in fig. 13 which is a tracing reduced to half size.

On the following pages are given the earlier mentioned tables and diagrams.

---

*) i. e. the values corresponding to 1.5 N and 1.0 N solutions.



Liquid : 0.888, N NaCl, I = 2.705 A
R_x = 1.36 Ω l = 187.2 mm
Temperature 28.00°C

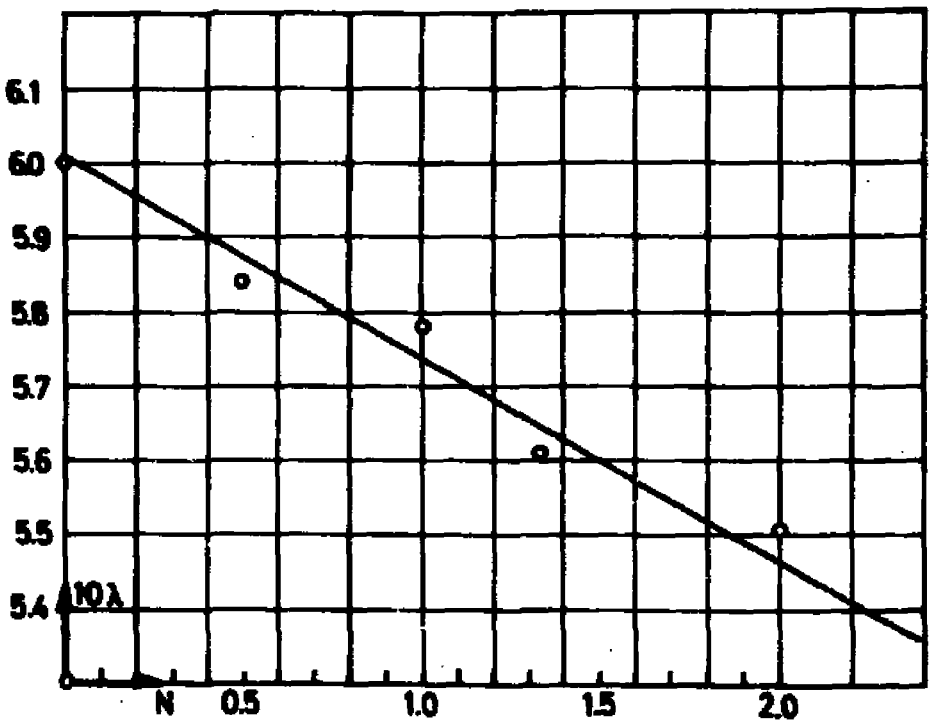
Fig.13

Table I

Measurements on aqueous KBr-solutions at 20.00°C

N equil. l^{-1}	ρ kgm^{-3}	c $J\,kg^{-1}\,{}^{o}C^{-1}$	$10\,\lambda$ $Wm^{-1}\,{}^{o}C^{-1}$	s %	s_{10} %
0.5020	1040	3893	5.84	1.02	0.32
1.010	1080	3684	5.78	0.83	0.26
1.341	1107	3571	5.61	1.02	0.32
2.013	1160	3349	5.51	1.88	0.60

Fig. 14 shows the measurement results from table I in graphical representation.



Measurements on K Br solutions from table I

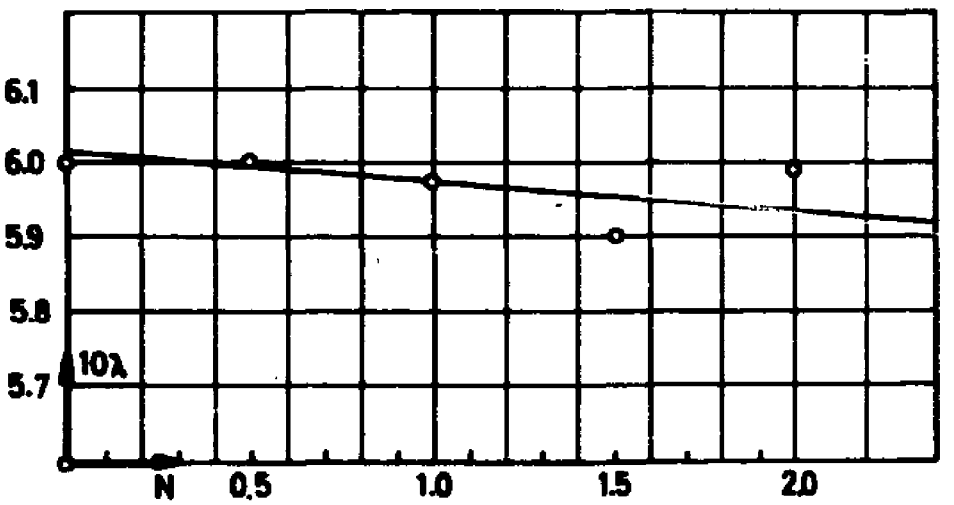
Fig. 14

Table II

Measurements on aqueous NaCl-solutions at 20.00°C

N equil. l^{-1}	ρ kgm^{-3}	c $J\,kg^{-1}\,{}^{o}C^{-1}$	$10\,\lambda$ $Wm^{-1}\,{}^{o}C^{-1}$	s %	s_{10} %
0.5032	1020	4033	6.01	1.26	0.40
1.010	1040	3911	5.97	0.60	0.19
1.510	1060	3803	5.90	1.31	0.41
2.009	1080	3695	5.99	0.92	0.29

Fig. 15 shows the measurement results from table II in graphical representation.



Measurements on Na Cl solutions from table II

Fig. 15

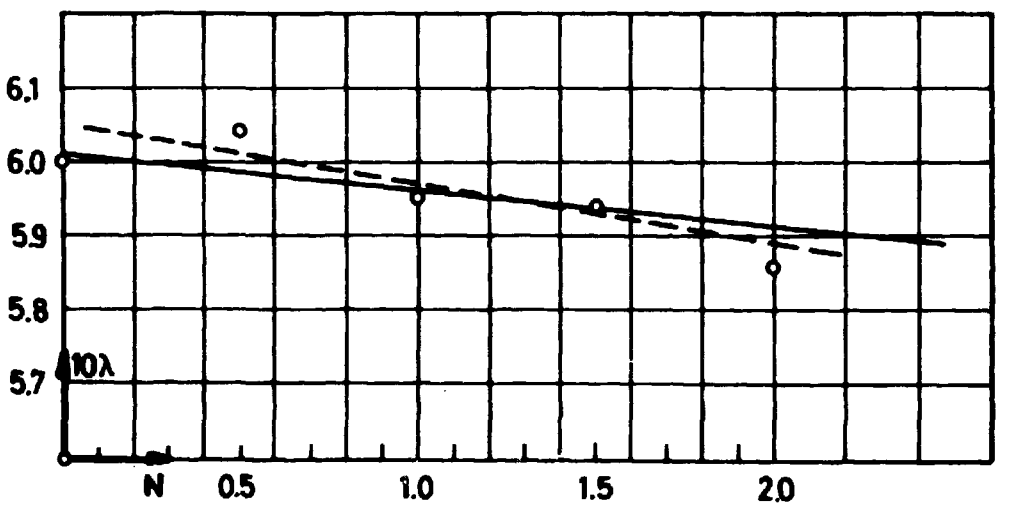
Table III

Measurements on aqueous $CuSO_4$-solutions at 20.00°C

N equil. l^{-1}	ρ kgm^{-3}	c $J\,kg^{-1}\,{}^{o}C^{-1}$	$10\,\lambda$ $Wm^{-1}\,{}^{o}C^{-1}$	s %	s_{10} %
0.5092	1039	3999	6.04	1.87	0.59
1.005	1078	3700	5.95	1.28	0.41
1.504	1116	3553	5.94	1.25	0.39
2.018	1154	3551	5.86	0.61	0.19

Fig. 16 shows the measurement results from table III in graphical representation.

The dashed line will be commented on shortly.



Measurements on $CuSO_4$ solutions from table III

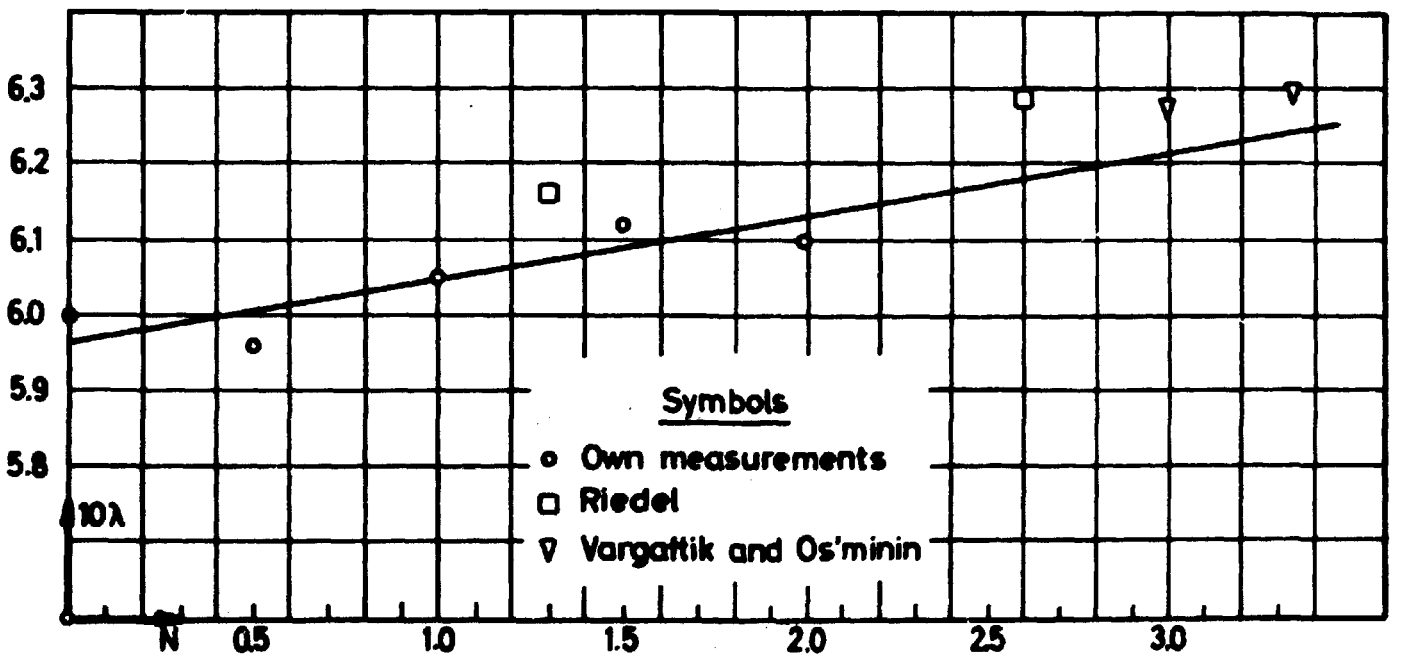
Fig. 16

Table IV

Measurements on aqueous NaOH-solutions at 20.00°C

N equil. l^{-1}	ρ kgm^{-3}	c $J\,kg^{-1}\,{}^{o}C^{-1}$	$10\,\lambda$ $Wm^{-1}\,{}^{o}C^{-1}$	s %	s_{10} %
0.5003	1020	4062	5.96	1.06	0.34
0.9987	1041	3975	6.05	0.85	0.27
1.496	1060	3914	6.12	1.85	0.58
1.985	1080	3852	6.10	1.00	0.32

Fig. 17 shows the measurement results from table IV in graphical representation. In the figure are further shown some values of other authors mentioned in the discussion to follow shortly.



Measurements on NaOH solutions from table IV

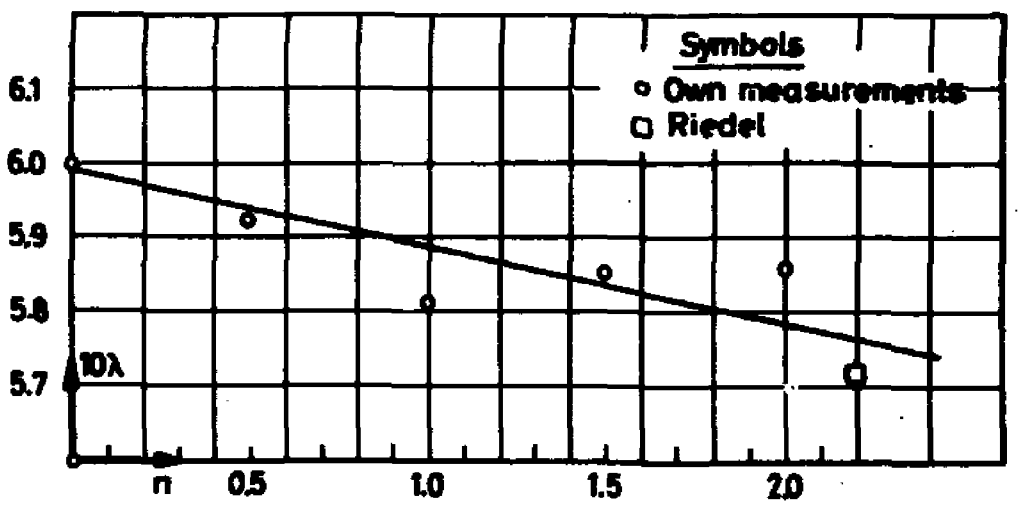
Fig.17

Table V

Measurements on aqueous H_2SO_4-solutions at 20.00°C

N equil. l^{-1}	ρ kgm^{-3}	c $J\,kg^{-1}\,°C^{-1}$	$10\,\lambda$ $Wm^{-1}\,°C^{-1}$	s %	s_{10} %
0.5050	1015	4081	5.92	0.54	0.17
1.007	1030	3998	5.81	1.86	0.59
1.507	1046	3914	5.85	0.71	0.23
2.013	1061	3880	5.86	1.18	0.37

Fig. 18 shows the measurements results from table V in graphical representation. In the figure is further included the value found by one other author.



Measurements on H_2SO_4 solutions from table V

Fig. 18

Finally the smoothed-out curves (straight lines) obtained from the tables are collected in fig. 19.

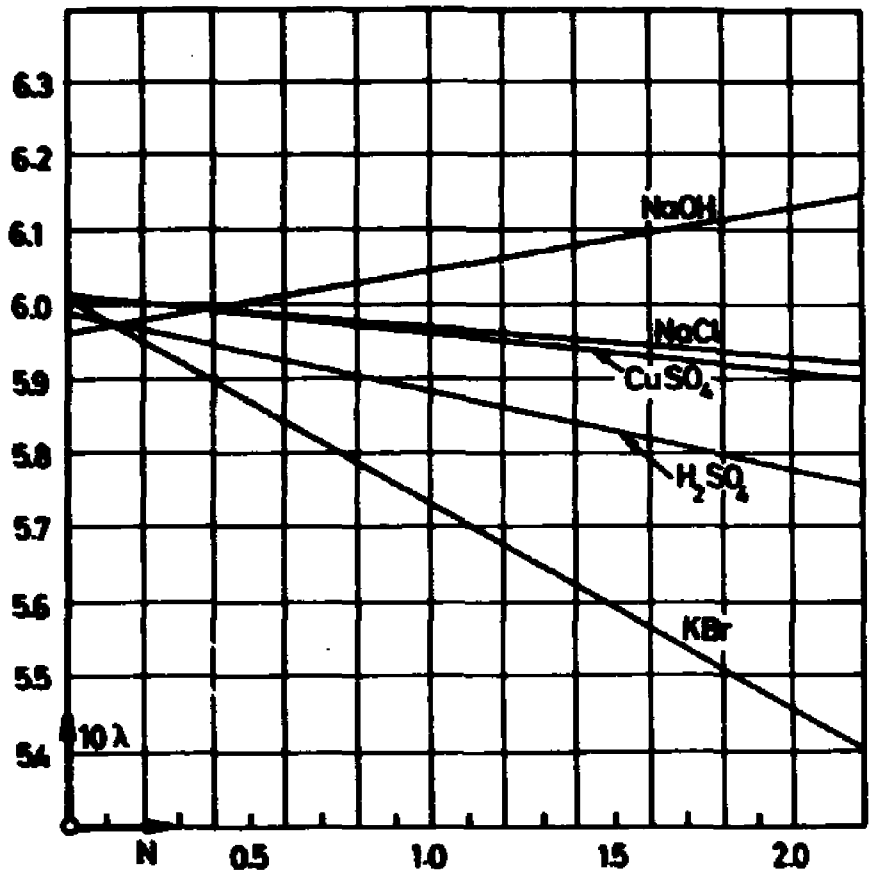


Fig. 19

4. Discussion of the Measurement Results

The distribution function satisfied by the 10 measurements on a given solution seems to be gaussian. This is indicated by the following. According to [7] we define the "limiting deviation" Δ as $\frac{1}{2}$ times the difference between the highest and the lowest value in a series of measurements. In [7] it is said *) that if such a series comprises 10 measurements, and if it is gaussian distributed, the mean value of $\frac{\Delta}{s}$ is 1.5, where Δ = the limiting deviation, and s, as before, = standard deviation. This test has with reasonable accuracy been passed by the series of measurements, at any rate when it is considered that $C^*_{H_2O}$ also has a small standard deviation. As mentioned before, that has been ignored in the s-values given in the tables. This is of course not quite correct.

---

*) On page 50.

As the standard deviations in the tables are often small, it might be expected that the individual points representing the mean values would in figs. 14-18 not be quite so much spread round the drawn straight lines which are intended to be first approximations to smoothed-out λ-N-curves.

It may not be quite correct to reckon with such first approximations. Alas [1] expressly states that the graphs are generally curved, and that they may deviate to both sides of the straight lined approximation. Alas uses second degree parabolas as approximations. However, Alas measures in a larger N-interval than has been done here, and generally the curvature only appears clearly in the last parts of Alas's intervals. We shall therefore estimate the distribution of the means using the straight lines in the figures although strictly speaking these curves ought perhaps to have a very small curvature.

When $\Delta\lambda$ are differences between λ-values (i. e. the means found) and $\frac{1}{10}$ of the ordinate of the straight line in the figure*) considered, we can, according to [7], page 91, estimate the standard deviation of the λ-values as being equal to a certain fraction of half the difference between the highest and the lowest value of $\Delta\lambda$ in the figure. This fraction is found in a table on page 50, op. cit., from which the value for $(\frac{\Delta}{s})_{mean}$ for a gaussian distributed series of 10 individual measurements was taken before. The fraction depends upon the number of the points. The number of points to be used in each figure may be a matter of discussion. One may stick to the 4 points that correspond to each their normality different from 0. On the other hand the apparatus is "calibrated" so that it gives 10 λ = 6 W/m ^{o}C when N = 0, and this has proved practicable with good reproducibility. As far as the author sees it, it must be possible to include such a "calibration" in the series considering it as equivalent to a measurement that gives (N, 10 λ) = (0, 6). If this is done, the mentioned table gives - with 5 points - that the standard deviation on the λ-values must be $\frac{1}{1.2}$ times the just mentioned "half difference". When it is borne in mind that these considerations are estimates, and that also $C^{*}_{H_2O}$ contributes slightly to the standard deviation of the means, it will be seen that the distribution of points in figures 14-18 must be said to be in reasonable agreement with the s_{10}-values given in the tables.

Finally the following comments can be made on figures Nos. 16 and 17:

---

*) One tenth, because the ordinate is 10 λ.

Fig. 16. The fully drawn line corresponds to the point (N, 10 λ) = (0, 6) having been included. The dashed line shows that the distribution of the other 4 points, when (0, 6) is not included, is very "smooth", but that λ_{H_2O} (corresponding to N = 0) is then found not quite 1% too high. Strangely enough there is actually a one-sided displacement of the results as compared with Alas's measurements on $CuSO_4$-solutions of this order of magnitude, and in this direction. As this is a question of thousandths, the explanation - or part of it - may be in the relatively inaccurate c-values for the $CuSO_4$-solutions mentioned before. (Alas does not need c-values in his corrections. At least only ρ-values are mentioned in [1].)

Fig. 17. The NaOH-solutions might have absorbed small quantities of CO_2 from the air in the bottles as for practical reasons they had to be left untouched for some time after preparation. At the termination of the work a random sample was taken, and it showed that the originally 0.5003 N solution was now 0.4915 N with respect to OH^- and 0.0088 N with respect to CO_3^{--}.

Altogether the results seem to be reasonably distributed within the series carried out at fixed normalities as well as in their dependence on the normalities.

Now only the question remains of their relation to the values of the literature.

As mention has so often been made of Alas's work [1], which i.a. contains measurements on KBr-, NaCl-, and $CuSO_4$-solutions, comparisons for these may suitably be made with [1]. Let λ_A be the λ-value stated in [1]*) corresponding to smoothed-out curves, and let λ_B be the λ-value given in the tables of the present work (i.e., measured values). With $\delta = 10^2(\lambda_A-\lambda_B)/\lambda_B$ we find for increasing normalities as they are given in tables I-III:

KBr-solutions: δ = 0.5, -0.6, 0.7, -0.5

NaCl-solutions: δ = -0.2, 0.2, 0.9, -1.0

$CuSO_4$-solutions: δ = -0.8, -0.9, -1.3, -0.9

---

*) As in [1] values are only stated relative to H_2O, λ_A has been found by multiplying these values by 0.6.

Alas compares his own values for all measured salt solutions with those of various other authors. With respect to Riedel's values he says that in some cases there is excellent agreement, and that in some cases the deviation is great (for $CaCl_2$ Alas finds values 1% higher than Riedel, and for KF Riedel's values are 1-2% higher than Alas's). Alas also quotes measurements made by Braune. Only in a few cases do they agree well with his own, and generally the deviations are greater than those from Riedel's values. Finally Alas states that measurements by Kapustinsky and Ruzavin are generally 1% above his own smoothed-out curves. When, in addition, we consider what was said generally in [2], section VII, about the agreement within the field that may be expected between the measurements of various authors, the agreement with the literature must be considered satisfactory in the case of the 3 salt solutions (tables I, II, and III).

As for the NaOH- and H_2SO_4-solutions there is only scant material in the literature. In the interval $0 \leq N \leq 2$ examined here, only those plotted in figs. 17 and 18 are known to the author. They also seem to indicate good agreement with the literature. The values given as Riedel's are those given by him in his editing of Landolt-Börnstein's λ-values, II Band, 5 Teil, 1968. This source must incidentally be considered the most comprehensive modern collection of values for λ for electrolytic solutions at different concentrations and temperatures*). For H_2SO_4, values for $N <$ approx. 2.2 and for NaOH, values for $N <$ approx. 1.3 are not given in Landolt-Börnstein's tables. The values for NaOH given as those of Vargaftik and Os'minin have been found in Gmelin's Handbuch, and they are said to have been obtained by a steady state method. They are valid at 29°C; but as λ_{NaOH} increases with temperature (cf. Riedel in Landolt-Börnstein, op. cit.), the values correspond to a slightly better agreement with the straight line in fig. 17 than shown.

*) At any rate this was the case at the conclusion of the present work in the middle of 1970.

ACKNOWLEDGEMENT

The author gratefully acknowledges the assistance given by many colleagues during the experiments described in this and the previous report. Individual names have been mentioned in the appropriate sections of the reports.

Appendix

As mentioned on page 17 it would be of considerable interest to be able to calculate the passing off of the pulses of current. This calculation involves, however, certain difficulties. From Maxwell's equations it is very easy to find the current density field $\vec{i}$ in wire and liquid if induction is neglected, i.e. if we put $\vec{E} = -\text{grad}\,\varphi$ ($\vec{E}$ = electric field, φ = voltage). The conductivity, σ, and the dielectric permeability, ε, are constant in the homogeneous bulk phases of the system *), and in these we find generally from the Maxwell equations

$$\frac{\partial}{\partial t}\left\{\vec{i} + \varepsilon \frac{\partial \vec{E}}{\partial t}\right\} = -\frac{1}{\mu_o}\,\text{rot rot}\,\vec{E} \quad ,$$

where μ_o is the magnetic permeability that may be put = the permeability in vacuum. If we thus put $\vec{E} = -\text{grad}\,\varphi$, we find

$$\frac{\partial}{\partial t}\left\{\vec{i} + \varepsilon \frac{\partial \vec{E}}{\partial t}\right\} \approx \vec{0} \quad ,$$

and if we use Ohm's law without a term originating from induction, i.e. if we put $\vec{i} = -\sigma\,\text{grad}\,\varphi$, we have

$$\frac{\partial}{\partial t}\left\{\vec{i} + \frac{\varepsilon}{\sigma}\frac{\partial \vec{i}}{\partial t}\right\} \approx \vec{0} \quad .$$

From this is found by integration using the designations from page 14

$$I^* = I_o^* e^{-\frac{t}{\tau^*}}$$

$$I_L = I_L^o e^{-\frac{t}{\tau}} \quad ,$$

where I_o^* and I_L^o are constants and

$$\tau^* = \frac{\varepsilon^*}{\sigma^*}$$

$$\tau = \frac{\varepsilon}{\sigma} \quad .$$

---

*) In the interfacial layers σ and ε are of course not constant.

Whether any real importance can be attached to the expressions found for I^* and I_L on the basis of the derivation given, depends upon the order of magnitude of τ and τ^*. If they are extremely small, the pulses of current should fade out extremely fast. But then the assumption that induction can be neglected is doubtful. We shall give an example that indicates the order of magnitude of τ and τ^*. $\varepsilon_{rel.}$ being equal to $\varepsilon/\varepsilon_0$, where ε_0 in the MKSA system has a value of approx. $9 \cdot 10^{-12}$ farads m^{-1}, and it being reasonable to put $\varepsilon_{rel.}$ for aqueous solutions $\simeq$ the value for water $\simeq$ 80, we have

$$\varepsilon = 80 \cdot 9 \cdot 10^{-12} \simeq 7 \cdot 10^{-10} \text{ farads } m^{-1}.$$

This gives, when σ is measured in $\Omega^{-1}\ m^{-1}$,

$$\tau \simeq \frac{7 \cdot 10^{-10}}{\sigma} \text{ seconds.}$$

If a 1 N KCl-solution at 25°C is taken as an example, we have $\sigma = 0.111134$ $\Omega^{-1}\ cm^{-1}$, i.e. σ = approx. 10 $\Omega^{-1}\ m^{-1}$. Consequently we find for this solution

$$\tau \simeq 10^{-10} \text{ seconds.}$$

Even a solution with 100 or 1000 times as small σ will thus show a very small τ-value, and stronger electrolytes have quite negligible τ-values.

For platinum σ is approximately $10^6 \cdot \sigma$ for the mentioned KCl-solution so that with a just fairly reasonable value of ε^* we will have $\tau^* \ll \tau$ for the KCl-solution $\simeq 10^{-10}$ seconds.

Thus it will be seen that the simple expressions derived for I^* and I_L must be considered doubtful unless they can be justified in some other way. The following is an example of the wrong results they may give: The derivation presupposes only homogeneous phases. $I^* = I_0^* e^{\frac{-t_0^*}{\tau^*}}$ must therefore for instance also be valid in the leads of a plate condenser during its charging. But it is well known that the passing off of its charging is not dependent solely on the properties of the lead material (i.e. on σ^* and ε^*). It depends on the resistance in the leads, the area of the plates, and the distance between these.

If an account is to be given of the passing off of the pulses of current,

apparently more complicated considerations must be used. As earlier mentioned, a later report on these matters is planned with the intention of investigating how far it is possible to pursue the phenomenon by calculation.

In this appendix the sole intention has been to point out that the simple calculation that one might be inclined to accept at first glance, is of doubtful value, and further that - as anticipated on page 14 - $\frac{\varepsilon}{\vartheta}$ and $\frac{\varepsilon}{\vartheta^2}$ are extremely small.

If a general calculation of the passing off of the current pulses could be carried out, the blank experiments would presumably be superfluous. For lack of such a calculation, the blank experiments, however, ensured the applicability of the modification. They have further shown that for electrolytic solutions it is not certain that one is always able to use the registrations immediately after the current is switched on (i. e. after some milliseconds). It might be desirable to be able to do so, so that disturbances due to convection could be disregarded beforehand. However, the investigations reported on in [2], concerning the convection during measurements, together with the blank experiments show that convection does not disturb even though the first registrations are cut away.

Finally it must be mentioned that the cutting away at the lower end of the diagrams has also been a presumption for the validity of the fairly simple system of formulas according to which λ is calculated. As the author sees it, the system of formulas becomes slightly more complicated if the basis is to be registrations corresponding to extremely short times after the switching on of the current.

References

[1]. Alas, Chiquillo, Messung der relativen Wärmeleitfähigkeit wässriger Salzlösungen nach einem instationären Hitzdrahtverfahren. Dissertation,Eidgenössische Technische Hochschule No. 3955 (Juris Verlag, Zürich, 1967) 77 pp.

[2]. Baruël, P., On Transient Hot-Wire Determination of the Thermal Conductivity of Pure, Dielectric Liquids. Risø Report No. 263 (1972).

[3]. Brønsted, J.N., Lærebog i fysisk kemi, 2. udgave. (Munksgaard, København, 1943) 498 pp.

[4]. Carslaw, H.S. and Jaeger, J.C., Conduction of Heat in Solids, 2nd edition (Clarendon Press, Oxford, 1959) 510 pp.

[5]. Eucken, A. and Englert, H., Z. ges. Kälteind. 45 (1938) 109-118.

[6]. Landau, L.D. and Lifshitz, E.M., Fluid Mechanics. (Pergamon Press, London, 1959) 536 pp.

[7]. Rasmussen, R.E.H., Elementær måleteori, 3. udgave. (Gjellerup, København, 1960) 131 pp.

[8]. Straumann, W., Ein instationäres Verfahren zur Messung der Wärmeleitfähigkeit von Flüssigkeiten und Gasen. Dissertation,Eidgenössische Technische Hochschule No. 3078. (Solothurn, Zürich, 1960) 27 pp.

[9]. Stålhane, B. and Pyk, S., Tekn. Tidsskrift A61 (1931) 389-393.

[10]. van der Held, E.F.M. and van Drunen, F.G., Physica 15 (1949) 865-881.

[11]. van der Held, E.F.M., Hardebol, J., and Kalshoven, J., Physica 19 (1953) 208-216.

Further the following collection of tables have been used:

Roth, Wather A. und Karl Scheel (editors), Landolt-Börnstein Physikalisch-Chemische Tabellen, 5. Auflage.(Springer, Berlin, 1923-36).

Gmelins Handbuch der anorganischen Chemie, 8. Auflage. (Verlag Chemie GMBH. Weinheim/Bergstr.).